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(21) International Application Number: PCT/US93/09821 (22) International Filing Date: 14 October 1993 (14.10.93) (30) Priority data: <table border="0" style="width: 100%;"><tr><td style="width: 33%;">07/961,269</td><td style="width: 33%;">14 October 1992 (14.10.92)</td><td style="width: 33%;">US</td></tr><tr><td>08/024,563</td><td>1 March 1993 (01.03.93)</td><td>US</td></tr><tr><td>08/055,063</td><td>28 April 1993 (28.04.93)</td><td>US</td></tr></table> (71) Applicant: THE DOW CHEMICAL COMPANY [US/US]; 2030 Dow Center, Abbott Road, Midland, MI 48640 (US). (72) Inventors: WALTON, Kim, L. ; 219 Huckelberry Drive, Lake Jackson, TX 77566 (US). PATEL, Rajen, M. ; 114 Scarlet Oak, Lake Jackson, TX 77566 (US). CHUM, Pak-Wing, Steve ; 126 Juniper Street, Lake Jackson, TX 77566 (US). OBLJESKI, Todd, J. ; 6061 Beverly Hill, Number 290, Houston, TX 77057 (US). WHITEMAN, Nicole, F. ; 323 Linden Lane, Lake Jackson, TX 77566 (US). MERGENHAGEN, Laura, K. ; 226 Acacia, Lake Jackson, TX 77566 (US).		07/961,269	14 October 1992 (14.10.92)	US	08/024,563	1 March 1993 (01.03.93)	US	08/055,063	28 April 1993 (28.04.93)	US	(74) Agent: WHITE, L., Wayne; The Dow Chemical Company, Patent Department, Building B-1211, Freeport, TX 77541-3257 (US). (81) Designated States: CA, FI, JP, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
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(54) Title: FILM FOR PACKAGING PURPOSES (57) Abstract Film and film-making methods with improved toughness, hot tack, shrinkability and extrusion processibility are disclosed for use in packaging and wrapping food, beverages and nonfood articles. The improved film comprises at least one layer of at least one substantially linear ethylene polymer, wherein the substantially linear ethylene polymer has a uniform branching distribution, and is also characterized as having essentially no linear polymer fraction, a single DSC melting peak and a density greater than 0.85 g/cm ³ . The films have utility in shrink, skin, stretch wrap, form-fill-seal and vacuum wrap operations.											

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FILM FOR PACKAGING PURPOSES

This invention relates to an improved packaging or wrapping film, and more particularly, to shrink, skin, stretch, hot tack, and vacuum wrap
5 films with improved clarity, toughness, extrusion processibility and irradiation cross-link efficiency. The films have at least one layer of at least one substantially linear ethylene polymer and may be biaxially oriented, multilayered and/or constructed with barrier characteristics. The substantially linear ethylene polymer is characterized as having a melt
10 flow ratio, $I_{10}/I_2 \geq 5.63$, a molecular weight distribution, M_w/M_n , defined by the equation: $M_w/M_n \geq (I_{10}/I_2) - 4.63$, and a critical shear rate at the onset of surface melt fracture of at least 50 percent greater than the critical shear rate at the onset of surface melt fracture of a linear ethylene polymer having about the same I_2 and M_w/M_n .

15 Food items and beverages such as poultry, vegetables, fresh red meat, wine, and cheese, as well as nonfood industrial and retail goods, are packaged by shrink, skin, stretch, form-fill-seal, bag-n-box and/or vacuum wrap methods. The shrink packaging method involves placing an article(s) into a bag fabricated from heat-shrinkable film material, then
20 closing or heat sealing the bag, and thereafter exposing the bag to sufficient heat to cause shrinking of the bag and intimate contact between the bag and article. The heat can be provided by conventional heat sources, such as heated air, infrared radiation, hot water, combustion flames, or the like. Shrink wrapping of food articles helps preserve
25 freshness, is attractive, hygienic, and allows closer inspection of the quality of the packaged food. Shrink wrapping of industrial and retail goods, which is alternatively referred to in the art and herein as industrial and retail bundling, preserves product cleanliness and also is a convenient means of bundling for accounting purposes.

30 The skin packaging method involves placing the product to be packaged on porous or perforated paperboard which is typically coated with an adhesive primer, then moving the loaded board to the platen of a skin packaging machine where a skin packaging film is heated until it softens and droops, relaxes and droops a second time over the loaded board. A
35 vacuum then draws the film down around the product to provide a "skin" tight package. Skin packaging serves both the consumer retail and the

transit markets. In the transit market, skin packaging protects industrial goods during transport and distribution. In the retail market, skin packaging protects consumer goods against damage and pilferage as well as provides "display appeal" to maximize the sales potential of the packaged product. While most, if not all, nonfood skin packaging film is monolayer, multilayer skin packaging films are useful for protecting food by vacuum packaging and, especially by vacuum skin packaging.

Film structures that provide rapid hot tack performance, hot tack films, are utilized to package food and non-food articles by the form-fill-seal process. In the form-fill-seal process, the film is folded or formed into a receiving pouch/bag by thermally sealing the layers of the film. Product is then immediately introduced into the formed bag and the resultant filled structure is sealed, typically by heat or ultrasound. The instant formed seal must withstand the force exerted as the product is loaded. In vertical form-fill-seal process, the product is dropped from a few centimeters above the loading area. Achieving rapid sealing or hot tack performance is critical to enabling line speeds to increase, without losing the integrity of the formed structure during the filling or loading operation.

Food items are also packaged by the stretch wrapping method which involves manually pulling a film over a paper pulp or foamed polystyrene tray filled with food (or automatically pushing the tray upward to stretch the film) and then heat sealing the stretched film at its edges usually on the underside of the tray, and allowing the film to remain taut due to its elasticity. For nonfood stretch wrapping, the stretch wrap film is manually or automatically pulled and stretched over and/or around the product, and thereafter the free end of the film is clung or tacked (rather than heat sealed) to another portion of film already wrapped about the product or to the product itself usually by applying pressure in the direction towards the product or goods being wrapped. Stretch wrap packaging of fresh food is specific to the consumer retail market and it allows fresh red meat to bloom to the desired bright red color as well as allows some vegetables to appropriately respire. Stretch wrapping of nonfood items corresponds to the transit market, and includes pallet wrapping of goods as well as wrapping of new vehicles during distribution

to protect exterior paint finishes from damage due to acid rain, road chips, debris, vandalism, etc.

Whereas stretch wrap packaging typically does not involve barrier film layers and is useful for both food and nonfood items, vacuum packaging involves a gas or oxygen barrier film layer and is generally reserved for red meats, processed meats and cheeses, but is also used to package odor-sensitive or odor-generating nonfood items such as cedar wood chips. There are several methods or variations of vacuum packaging including vacuum skin packaging which is also referred to in the art as vacuum form packaging. One method involves, for example, bringing a heat-softened top and bottom film web together under vacuum in a chamber with the product loaded between the webs; thereafter, heat sealing the webs together at their edges, and then evacuating or gas flushing the space containing the product. In vacuum packaging, typically the bottom web takes up the form of the food item being packaged.

While the shrink wrapping method is predicated on the heat-shrinking properties of the selected film materials, stretch overwrapping is predicated on the elasticity of the film material. Conversely, successful skin packaging is predicated on the adhesion of the film material to the primed board and the amount of time required to cause the film to double droop (cycle time). Similar to skin packaging, successful vacuum packaging depends on the time required for the film webs to sufficiently soften before being drawn by vacuum (or pushed by air pressure) about the product to be packaged. As taught in Plastics Design and Processing, November 1980, page 4, film materials with more infra-red heat absorption bands and/or with a lower Vicat softening point will tend to heat-up and soften faster, and thereby allow faster cycle times in skin and vacuum packaging. In general, polar polymers such as, for example, ethylene vinyl acetate (EVA) copolymers, ethylene acrylic acid (EAA) copolymers and ionomers, will possess more infra-red heat bands than nonpolar polymers such as the substantially linear ethylene polymers of the present invention or heterogeneous LLDPE. Further, ionomers show more infra-red heat bands than their respective base copolymers due the ionomerization itself.

Successful packaging or wrapping for all four methods, depends on the toughness and abuse or implosion resistance properties of the film

materials themselves such that the packaged product's integrity is maintained during distribution, handling and/or display. However, toughness and abuse resistance are particularly important in food shrink wrapping and vacuum packaging which often times involves packaging of meat
5 and other food cuts with deep cavities and sharp exposed bones as well as exposed edges that can puncture the film webs or fabricated bag during the heat-shrink or vacuuming-form operation or during subsequent package handling and distribution. To avoid premature puncturing, film producers resort to expensive practices to toughen the package such as using thicker
10 films and bags, using an extra layer of film at critical contact points of the bag in a patch-like fashion as described by Ferguson in US Patent 4,755,403, or by using cross-ply or non-parallel layer constructions. Similarly, to "artificially" enhance the puncture and other abuse or implosion resistance characteristics of known film materials, food
15 packagers routinely wrap or cap exposed bone edges with cloth, molded plastic articles or other materials.

An important shrink bundling and skin packaging property, particularly for delicate items or items which tend to crush or bend, such as paper goods, is the tension or force the film exerts on the packaged
20 article and/or board. This attribute is known in the art as shrink tension, and films with too much shrink tension invariably yield shrink or skin packages with unsightly buckling or board curl that in severe cases can render the packaged good unusable for its intended purpose. In addition to being aesthetically unsightly, buckled or warped goods are
25 difficult to stack uniformly on display shelves.

The film optical properties are also important for retail "point-of-purchase" shrink, skin, stretch and vacuum wrap packages. The better the contact and/or see-through clarity, the lower internal film haze and the higher film gloss or sparkleness, the more likely the package will attract
30 a potential purchaser for closer inspection. Further, consumers generally associate the package aesthetics, which are chiefly predicated on the optical properties of the packaging film, directly with the quality of the article to be purchased.

Another important retail "point-of-purchase" requirement, that is
35 specific to stretch wrapping, is the ability of the film to "snap back" when deformed rather than retain the dents and impressions left from

inspections by prospective purchasers. This attribute is predicated on the elastic recovery of the film material, and when elastic recovery is sufficiently high, subsequent prospective purchasers are not unnecessarily prejudiced by the package appearing as if it had been handled and
5 repeatedly rejected.

Still another important film material characteristic, that can affect the overall success of all four packaging and wrapping methods, is the extrusion processibility of the film resin during film fabrication by well known bubble, cast or sheet extrusion methods. Good processibility
10 is manifested as relatively low extrusion energy consumption, a smoother film surface and as a stable bubble or web even at higher blow-up ratios, draw rates and/or film thicknesses. There are numerous benefits of a smoother, more stable film-making operation, including film widths and thicknesses are generally more uniform, the need to edge trim is reduced
15 (which reduces waste), winding and unwinding operations are typically smoother, there are fewer film wrinkles, and the final package quality or appearance is improved.

While high pressure polymerized ethylene homopolymers and copolymers, such as low density polyethylene (LDPE) and ethylene vinyl
20 acetate (EVA) copolymers, generally exhibit good processibility during extrusion as the consequence of having relatively high degrees of long chain branching, linear olefin polymers such as linear low density polyethylene (LLDPE) and ultra low density polyethylene (ULDPE), which is alternatively known in the art as very low density polyethylene (VLDPE),
25 show fair-to-marginal processibility even when fairly sophisticated extrusion screw designs are employed such as barrier screws, screws with Maddock mixing sections, and other like variations are employed to better homogenize or stabilize the polymer melt stream and allow lower energy consumption and smoother polymer surfaces. Further, in attempts to
30 maximize the toughness characteristics of known EVA, ULDPE and LLDPE materials, it is common practice to employ very high molecular weight grades, for example melt indices (I_2 , as measured in accordance with ASTM D-1238 (190°C/2.16kg)) of ≥ 0.5 g/10 minutes, which inevitably adds to processibility difficulties.

35 To meet the diverse performance requirements involved in all five packaging and wrapping methods, various film materials have been used as

single components and in blended combinations for both monolayer and multilayer packaging. For example, Smith in US Patent 5,032,463 discloses biaxially stretched monolayer and multilayer films comprising blends of ethylene/1-butene ultra low density polyethylene and ethylene/1-hexene
5 ultra low density polyethylene.

As another example, Lustig et al. in US Patent 5,059,481 describe biaxially oriented ultra low density polyethylene monolayer and multilayer packaging films with a barrier core layer, an ethylene/vinyl acetate intermediate layer and ULDPE/EVA blends as the outer layer. In US Patent
10 4,863,769, Lustig et al. disclose the use these biaxially oriented ultra low density films as bags for packaging frozen poultry, and in US Patent 4,976,898, Lustig et al. disclose that the "double bubble" method can be used to prepare the biaxially oriented ultra low density polyethylene films.

15 In another example, Botto et al. in European Patent Application 0 243 510 describes a multilayer skin packaging film consisting of an ionomer, EVA and HDPE that is particularly useful for vacuum skin packaging of food.

While prior art film materials have varying degrees of toughness,
20 implosion resistance, low temperature shrinking characteristics, and bag making heat sealing performances, even tougher film materials are desired in shrink, skin and vacuum packaging for reduced bag punctures or for maintaining puncture resistance levels when down-gauging film thicknesses for environmental source reduction purposes, cost-effectiveness or other
25 considerations. Moreover, while LDPE produced via free radical, high pressure polymerization of ethylene performs satisfactorily in industrial (transit) shrink and skin packaging applications, the optical properties of LDPE generally are not satisfactory for consumer retail packaging applications and in the instance of retail skin packaging, packagers are
30 left to rely on expensive film materials, such as Surlyn® ionomers supplied by E. I duPont, for the desired optical appeal. However, even the expensive ionomer products show skin packaging deficiencies such as poor biaxial tear/cut resistance and insufficient drawability that can yield aesthetically unpleasing ridges and/or bridges when multiple items
35 are packaged on a single paperboard.

Although having poor tear/cut resistance in both the machine and transverse directions is clearly an ionomer disadvantage, there is benefit to reduced tear/cut resistance in one direction or other, that is, to facilitate easy opening of the package while maintaining its tamper-evident quality.

The search for an alternative to polyvinyl chloride (PVC) films for stretch wrap for food is another example of packagers having to rely on expensive film materials. Such alternatives have typically been olefin multilayer film. The search is important, however, because PVC has undesirable plasticizer migration tendencies as well as a growing environmental concern regarding chlorinated polymers in general. While various multilayer films have been disclosed (for example, in US Patent 5,112, 674 and US Patent 5,006,398, and in EPO 0 243 965, EPO 0 333 508, and EPO 0 404 969) with similar snap-back or elastic recovery as PVC, many of these solutions involve coextrusions with ethylene copolymers such as EVA and ethylene acrylic acid (EAA) copolymers. However, the use of these polar copolymers presents processing limitations that include thermal instability and recycle/trim incompatibility.

Another desired improvement over known olefin polymers is disclosed in EPO 0 404 368 where Ziegler catalyzed ethylene α -olefin copolymers, such as ethylene/1-butene, ethylene/1-hexene, and ethylene/1-octene copolymers are shown to require blending with LDPE to provide film materials with adequate shrink properties (especially in the cross direction) when processed via simple hot blown bubble film extrusion.

In providing film materials with improved toughness and abuse or implosion resistance characteristics for shrink packaging, good low temperature heat-shrink performance in both the machine and cross directions must also be provided. Also, for shrink and skin packages void of excessive curl or warpage, shrink tension must be maintained at a low level, and to achieve the desired free shrink characteristics, the film material must possess the morphology and be strong enough to withstand the physical biaxial stretching that occurs during film fabrication in the simple bubble extrusion process or in more elaborate processes such as the double bubble process described by Pahlke in US Patent 3,555,604. Improved film materials must also exhibit good processibility and optical properties relative to known film materials, and particularly, relative to

the VLDPE materials and films disclosed by Lustig et al. in US Patent 5,059,481; US Patent 4,863,769; and US Patent 4,976,898.

Mitsui Petrochemical has been selling products prepared by polymerizing ethylene and a higher α -olefin under the trademark "Tafmer®" for more than a decade that are considered to be a class of very low modulus VLDPE materials. Some of the Tafmer® grades have been marketed for use in multilayer film packaging structures. For example, US Patent 4,429,079 (Shibata et al.) assigned to Mitsui Petrochemical Industries, discloses a composition in which a random ethylene copolymer (conventional LLDPE having one, two or more melting points from 115°C to 130°C labeled as component (A) is blended with another random ethylene copolymer (one having a single melting point from 40°C to 100°C), labeled as component (B) to provide compositions where component (B) does not exceed 60 percent by weight of the total composition with improved properties, in particular, improved low-temperature heat sealability and flexural toughness for resisting pinhole formation during handling. However, with excellent heat sealability and flexibility notwithstanding, Tafmer® products are not generally recognized or marketed as having excellent abuse resistance properties and shrink characteristics. The Tafmer® products having a single melting point are homogeneously branched linear polyethylenes which were earlier described by Elston in US Patent 3,645,992 and are made by a related polymerization process using vanadium catalysts.

Exxon Chemical Company has recently introduced products similar to Mitsui Petrochemical's Tafmer® products which Exxon prepared by polymerizing ethylene and an α -olefin (for example, 1-butene or n-hexene) in the presence of a single site metallocene catalyst. In a paper presented on September 22-27, 1991 at the 1991 IEEE Power Engineering Society Transmission and Distribution Conference ("New Specialty Linear Polymers (SLP) For Power Cables", printed in the proceedings on pp. 184-190) in Dallas, Texas, Monica Hendewerk and Lawrence Spenadel, of Exxon Chemical Company, reported that Exxon's Exact® polyolefins polymers, said to be produced using single site metallocene catalyst technology, are useful in wire and cable coating applications. Also, in the 1991 Polymers, Laminations & Coatings Conference Proceedings, pp. 289-296 ("A New Family of Linear Ethylene Polymers Provides Enhanced Sealing

Performance" by Dirk G. F. Van der Sanden and Richard W. Halle, (also published in February 1992 TAPPI Journal)), and in ANTEC '92 Proceedings, pp. 154-158 ("Exact& Linear Ethylene Polymers for Enhanced Sealing Performance" by D. Van der Sanden and R.W. Halle) Exxon Chemical describe
5 their new narrow molecular weight distribution polymers made using a single site metallocene catalyst as "linear backbone resins containing no functional or long chain branches." Films made from the polymers produced by Exxon are also said to have advantages in sealing characteristics as measured by hot-tack and heat-seal curves, but these publications do not
10 discuss shrink characteristics. The new Exxon polymers are said to be linear and to have narrow molecular weight distributions, and, because of the narrow molecular weight distribution, are also said to have "the potential for melt fracture." Exxon Chemical acknowledged that "it is well known that narrow-MWD polymers are somewhat more difficult to
15 process."

Accordingly, although new materials have been recently developed and marketed for flexible packaging or wrapping purposes, the need still exists for improved olefin packaging films and bags or wraps fabricated therefrom, with particular improvement needed in regard to recovery,
20 shrink characteristics, hot tack, vacuum drawability abuse or implosion resistance and processibility relative to the VLDPE olefin polymers with linear backbones such as those described by Lustig et al. in US Patent 4,863,769; US Patent 4,976,898 and US Patent 5,059,481.

In accordance with the present invention, we have discovered a new
25 and improved:

(A) wrapping or packaging film suitable for use in fabricating bags and wraps for packaging food, beverage and nonfood articles by the shrink, skin, stretch, form-fill-seal and vacuum packaging methods, wherein said film comprises at least one layer of at least one substantially linear
30 ethylene polymer,

(B) method of making a shrink film structure having both machine direction and transverse direction shrinkage by using conventional hot blown film manufacturing techniques wherein the method comprises the steps of:

35 (i) extruding at least one substantially linear ethylene polymer into at least one layer of an extrudate,

(ii) passing the extrudate of (i) through an annular die to form a tubular film, and

5 (iii) blowing the tubular film from (ii) into the film structure.

(C) method of making oriented wrapping or packaging film comprising the steps of:

10 (i) extruding at least one substantially linear ethylene polymer into an extrudate,

(ii) passing the extrudate of (i) through an annular die to form a primary tube film,

15 (iii) heating the primary tube film of (ii),

(iv) orienting the heated primary tube film of (iii).

20 Optionally, step (iv) can be accomplished by using a biaxial orientation technique such as a double bubble method, a tenter frame or a high blow-up (BUR) technique, or combination thereof.

25 Also optionally, the primary tube film of (iii) can be irradiated before and/or after the orientation step of (iv).

The film and film-making improvements are achieved by using a substantially linear ethylene polymer which is characterized as having:

- 30 i. a melt flow ratio, $I_{10}/I_2 \geq 5.63$,
- ii. a molecular weight distribution, M_w/M_n , defined by the equation: $M_w/M_n \geq (I_{10}/I_2) - 4.63$, and
- 35 iii. a critical shear rate at the onset of surface melt fracture of at least 50 percent greater than the critical shear rate at the onset of surface melt

fracture of a linear ethylene polymer having about the same I_2 and M_w/M_n .

The new films represent, in particular, an improvement over the
5 film, the film-making method and the packaging bag or wrap disclosed by Lustig et al. in US Patent 5,059,481; US Patent 4,863,769; and US Patent 4,976,898; by Smith in US Patent 5,032,463; by Parnell et al. in US Patent 5,041,316 and by Quacquarella et al. in US Patent 4,801,486.

The substantially linear ethylene homopolymers and interpolymers
10 used in the present invention are a unique class of compounds that are further defined in copending US application serial number 07/776,130 filed October 15, 1991 and in copending US application serial number 07/939,281 filed September 2, 1992.

These unique substantially linear ethylene homopolymers and
15 interpolymers are not in the same class as the conventional homogeneously branched linear ethylene/ α -olefin copolymers described in US Patent 3,645,992 (Elston) nor are they in the same class as conventional Ziegler polymerized linear ethylene/ α -olefin copolymers (for example, linear low density polyethylene or linear high density polyethylene made, for
20 example, using the technique disclosed by Anderson et al. in US Patent 4,076,698), nor are they in the same class as traditional highly branched LDPE. The substantially linear ethylene homopolymers and interpolymers useful in this invention have excellent processability, even though they have relatively narrow molecular weight distributions and exhibit good
25 shrink characteristics when made into film and biaxially stretched or oriented by the less elaborate simple bubble fabrication method. Even more surprisingly, the melt flow ratio (I_{10}/I_2) of the substantially linear ethylene homopolymers or interpolymers can be varied essentially independently of the polydispersity index (that is, the molecular weight
30 distribution, M_w/M_n). This behavior is a contradistinction to the linear ethylene/ α -olefin copolymers described by Elston and to the conventional Ziegler polymerized linear polyethylene copolymers having rheological properties such that as the polydispersity index increases, the I_{10}/I_2 value also increases.

35 The term "substantially linear" means that the polymer backbone is substituted with 0.01 long chain branches/1000 carbons to 3 long chain

branches/1000 carbons, more preferably from 0.01 long chain branches/1000 carbons to 1 long chain branches/1000 carbons, and especially from 0.05 long chain branches/1000 carbons to 1 long chain branches/1000 carbons.

Long chain branching is defined herein as a chain length of at least
5 6 carbons, above which the length cannot be distinguished using ^{13}C nuclear magnetic resonance spectroscopy, yet the long chain branch can be about the same length as the length of the polymer back-bone.

Long chain branching is determined by using ^{13}C nuclear magnetic resonance (NMR) spectroscopy and is quantified using the method described
10 by Randall (Rev. Macromol. Chem. Phys., C29, V. 2&3, p. 285-297).

The substantially linear homopolymers for use in making the improved biaxially oriented, heat-shrinkable film and bag of the present invention are polymers of ethylene involving no additional monomer or comonomer although at least one chain transfer agent may be employed to affect
15 polymer molecular characteristics. The substantially linear ethylene interpolymers for use in making the improved biaxially oriented, heat-shrinkable film of the present invention are interpolymers of ethylene with at least one $\text{C}_3\text{-C}_{20}$ α -olefin and/or $\text{C}_4\text{-C}_{18}$ diolefin. Copolymers of ethylene and an α -olefin of $\text{C}_3\text{-C}_{20}$ carbon atoms are especially preferred.
20 The term "interpolymer" is used herein to indicate a copolymer, or a terpolymer, or the like, where, at least one other comonomer is polymerized with ethylene to make the interpolymer.

Suitable unsaturated comonomers useful for polymerizing with ethylene include, for example, ethylenically unsaturated monomers,
25 conjugated or non-conjugated dienes, polyenes, etc. Examples of such comonomers include $\text{C}_3\text{-C}_{20}$ α -olefins as propylene, isobutylene, 1-butene, 1-hexene, 4-methyl-1-pentene, 1-heptene, 1-octene, 1-nonene, 1-decene. Preferred comonomers include propylene, 1-butene, 1-hexene, 4-methyl-1-pentene and 1-octene, and 1-octene is especially preferred. Other
30 suitable monomers include styrene, halo- or alkyl-substituted styrenes, tetrafluoroethylene, vinylbenzocyclobutane, 1,4-hexadiene, 1,7-octadiene, and cycloalkenes, for example, cyclopentene, cyclohexene and cyclooctene.

The density of the substantially linear ethylene interpolymers or homopolymers (as measured in accordance with ASTM D-792) for use in the
35 present invention is generally greater than 0.85 g/cm^3 , especially from

0.86 g/cm³ to 0.93 g/cm³, more preferably, from 0.88 g/cm³ to 0.92 g/cm³, and as high as 0.965 g/cm³.

The molecular weight of the substantially linear ethylene interpolymers or homopolymers is conveniently indicated using a melt index measurement according to ASTM D-1238, Condition 190°C/2.16 kg (formerly known as "Condition E" and also known as I₂). Melt index is inversely proportional to the molecular weight of the polymer. Thus, the higher the molecular weight, the lower the melt index, although the relationship is not linear. The melt index for the substantially linear ethylene interpolymers and homopolymers useful herein is generally from 0.01 g/10 min. to 10 g/10 min., preferably from 0.01 g/10 min. to 3 g/10 min., and especially from 0.1 g/10 min. to 2 g/10 min.

Other measurements useful in characterizing the molecular weight of substantially linear ethylene interpolymers and homopolymers involve melt index determinations with higher weights, such as, for common example, ASTM D-1238, Condition 190°C/10 kg (formerly known as "Condition N" and also known as I₁₀). The ratio of a higher weight melt index determination to a lower weight determination is known as a melt flow ratio, and for measured I₁₀ and the I₂ melt index values the melt flow ratio is conveniently designated as I₁₀/I₂. For the substantially linear ethylene interpolymers and homopolymers used to prepare the films of the present invention, the melt flow ratio indicates the degree of long chain branching, that is, the higher the I₁₀/I₂ melt flow ratio, the more long chain branching in the polymer. The I₁₀/I₂ ratio of the substantially linear ethylene interpolymers and homopolymers is preferably at least 7, especially at least 9, and can be as high as 50.

Additives such as antioxidants (for example, hindered phenolics such as Irganox® 1010 or Irganox® 1076 supplied by Ciba-Geigy), phosphites (for example, Irgafos® 168 supplied by Ciba-Geigy), cling additives (for example, PIB), PEPQ® (a trademark of Sandoz Chemical, the primary ingredient of which is believed to be a biphenylphosphonite), pigments, colorants, fillers also be included in the interpolymers and copolymers, to the extent that they do not interfere with the enhanced film properties discovered by Applicants. The fabricated film may also contain additives to enhance its antiblocking and coefficient of friction characteristics including, but not limited to, untreated and treated silicon dioxide,

talc, calcium carbonate, and clay, as well as primary and secondary fatty acid amides, silicone coatings, etc. Other additives to enhance the film's anti-fogging characteristics may also be added, as described, for example, in US Patent 4,486,552 (Niemann). Still other additives, such as
5 quaternary ammonium compounds alone or in combination with EAA or other functional polymers, may also be added to enhance the film's antistatic characteristics and allow packaging of electronically sensitive goods.

The substantially linear ethylene interpolymers or homopolymers used to prepare the olefin packaging and wrapping films of the present
10 invention can be used as the only polymer component of the film whether the structure to be used is a monolayer or multilayer construction. Other polymers can also be blended with the substantially linear ethylene interpolymers or homopolymers to modify the film processing, film strength, heat seal, or adhesion characteristics. Packaging and wrapping
15 films made with appropriate blends of the substantially linear ethylene interpolymers or homopolymers and other polymer components maintain enhanced performance and in specific instances can offer improved combinations of properties. Some useful materials for blending with substantially linear ethylene interpolymers and homopolymers include, for
20 example, but are not limited to, high pressure low density polyethylene (LDPE), ethylene/vinyl acetate copolymer (EVA), ethylene/carboxylic acid copolymers and ionomers thereof, polybutylene (PB), and α -olefin polymers such as high density polyethylene, medium density polyethylene, polypropylene, ethylene/propylene interpolymers, linear low density
25 polyethylene (LLDPE) and ultra low density polyethylene, as well as graft-modified polymers, and blends thereof including variation in density, MWD, and/or comonomer combinations such as those disclosed, for example, by Smith in US Patent 5,032,463 which is incorporated herein by reference. However, preferably the substantially linear ethylene interpolymer or
30 homopolymer comprise at least 50 percent of the blend composition, more preferably at least 80 percent of the blend composition. Highly preferably, though, for multilayer film constructions, the outer film layers (alternatively referred to in the art as "skin layers" or "surface layers") and the sealant layers would consist essentially of the
35 substantially linear ethylene interpolymer and/or homopolymer.

The "rheological processing index" (PI) is the apparent viscosity (in kpoise) of a polymer measured by a gas extrusion rheometer (GER). The gas extrusion rheometer is described by M. Shida, R.N. Shroff and L.V. Cancio in Polymer Engineering Science, Vol. 17, No. 11, p. 770 (1977), and
5 in "Rheometers for Molten Plastics" by John Dealy, published by Van Nostrand Reinhold Co. (1982) on pp. 97-99, both publications of which are incorporated by reference herein in their entirety. GER experiments are performed at a temperature of 190°C, at nitrogen pressures between 250 to 5500 psig using a 7.54 cm diameter, 20:1 L/D die with an entrance angle of
10 180°. For the substantially linear ethylene polymers described herein, the PI is the apparent viscosity (in kpoise) of a material measured by GER at an apparent shear stress of 2.15×10^6 dyne/cm². The novel substantially linear ethylene interpolymers and homopolymers described herein preferably have a PI in the range of 0.01 kpoise to 50 kpoise,
15 preferably 15 kpoise or less. The novel substantially linear substantially linear ethylene interpolymers and homopolymers described herein have a PI less than or equal to 70 percent of the PI of a comparative linear ethylene polymer (either a Ziegler polymerized polymer or a linear uniformly branched polymer as described by Elston in US Patent
20 3,645,992) at about the same I_2 and M_w/M_n .

To more fully characterize the rheological behavior of the unique substantially linear ethylene polymers, S. Lai and G.W. Knight recently introduced (ANTEC '93 Proceedings, INSITE™ Technology Polyolefins (ITP) - New Rules in the Structure/Rheology Relationship of Ethylene α -Olefin
25 Copolymers, New Orleans, La., May 1993) another rheological measurement, the Dow Rheology Index (DRI), which expresses a polymer's "normalized relaxation time as the result of long chain branching." DRI ranges from 0 for polymers which do not have any measurable long chain branching (e.g., Tafmer™ and Exact™ products) to about 15 and is independent of melt
30 index. In general, for low to medium pressure ethylene polymers (particularly at lower densities) DRI provides improved correlations to melt elasticity and high shear flowability relative to correlations of the same attempted with melt flow ratios, and for the substantially linear ethylene polymers of this invention, DRI is preferably at least about 0.1,
35 and especially at least about 0.5, and most especially at least 0.8. DRI can be calculated from the equation:

$$DRI = (3652879 * \tau_o^{1.00649} / \eta_o - 1) / 10$$

5 where τ_o is the characteristic relaxation time of the material and η_o is the zero shear viscosity of the material. Both τ_o and η_o are the "best fit" values to the Cross equation, i.e.

$$\eta / \eta_o = 1 / (1 + (\dot{\gamma} * \tau_o)^{1-n})$$

10 where n is the power law index of the material, and η and $\dot{\gamma}$ are the measured viscosity and shear rate, respectively. Baseline determination of viscosity and shear rate data are obtained using a Rheometric Mechanical Spectrometer (RMS-800) under dynamic sweep mode from 0.1 to 100 radians/second at
15 160°C and a Gas Extrusion Rheometer (GER) at extrusion pressures from 1,000 psi to 5,000 psi (6.89 to 34.5 MPa), which corresponds to shear stress from 0.086 to 0.43 MPa, using a 7.54 centimeter diameter, 20:1 L/D die at 190°C. Specific material determinations can be performed from 140 to
20 190°C as required to accommodate melt index variations.

An apparent shear stress versus apparent shear rate plot is used to identify the melt fracture phenomena. According to Ramamurthy in the Journal of Rheology, 30(2), 337-357, 1986, above a certain critical flow
25 rate, the observed extrudate irregularities may be broadly classified into two main types: surface melt fracture and gross melt fracture.

Surface melt fracture occurs under apparently steady flow conditions and ranges in detail from loss of specular film gloss to the more severe form of "sharkskin." In this disclosure, the onset of surface melt
30 fracture (OSMF) is characterized at the beginning of losing extrudate gloss at which the surface roughness of the extrudate can only be detected by 40x magnification. The critical shear rate at the onset of surface melt fracture for the substantially linear ethylene interpolymers and homopolymers is at least 50 percent greater than the critical shear rate
35 at the onset of surface melt fracture of a comparative linear ethylene polymer (either a Ziegler polymerized polymer or a linear uniformly

branched polymer as described by Elston in US Patent 3,645,992) having about the same I_2 and M_w/M_n .

Gross melt fracture occurs at unsteady extrusion flow conditions and ranges in detail from regular (alternating rough and smooth, helical, etc.) to random distortions. For commercial acceptability, (for example, in blown films and bags therefrom), surface defects should be minimal, if not absent, for good film quality and properties. The critical shear stress at the onset of gross melt fracture for the substantially linear ethylene interpolymers, especially those having a density >0.91 g/cm³, and homopolymers used in making the biaxially oriented, heat-shrinkable film of the present invention is greater than 4×10^6 dynes/cm². The critical shear rate at the onset of surface melt fracture (OSMF) and the onset of gross melt fracture (OGMF) will be used herein based on the changes of surface roughness and configurations of the extrudates extruded by a GER.

Substantially linear ethylene polymers are homogeneous have a homogeneous branching distribution, as defined in US Patent 3,645,992, wherein substantially all of the copolymer molecules have the same ethylene-to-comonomer ratio and the polymer is characterized by a narrow short chain branching distribution where the short chain branching index (defined herein below) is greater than 30 percent, more preferably greater than 50 percent, and (4) the polymer essentially lacks a measurable high density (crystalline) polymer fraction as measured by known fractionation techniques such as, for example, a method that involves polymer fractional elutions as a function of temperature.

Substantially linear ethylene copolymers are considered to be "homogeneous" since substantially all of the copolymer molecules have the same ethylene-to-comonomer ratio. Moreover, substantially linear ethylene polymers have a narrow short chain (homogeneous) branching distribution, as defined by US Patent 3,645,992. The distribution of comonomer branches for the substantially linear ethylene polymers is characterized by its SCBDI (Short Chain Branch Distribution Index) or CDBI (Composition Distribution Branch Index) and is defined as the weight percent of the polymer molecules having a comonomer content within 50 percent of the median total molar comonomer content. The CDBI of a polymer is readily calculated from data obtained from techniques known in the art, such as, for example, temperature rising elution fractionation (abbreviated herein

as "TREF") as described, for example, by Wild et al., Journal of Polymer Science, Poly. Phys. Ed., Vol. 20, p. 441 (1982), or in US Patent 4,798,081, both disclosures of which are incorporated herein by reference. The SCBDI or CDBI for the substantially linear interpolymers and
5 homopolymers of the present invention is preferably greater than 30 percent, especially greater than 50 percent.

The substantially linear ethylene interpolymers and homopolymers used in this invention essentially lack a measurable "high density" fraction as measured by the TREF technique. The substantially linear
10 interpolymers and copolymers do not contain a polymer fraction with a degree of branching less than or equal to 2 methyls/1000 carbons. The "high density polymer fraction" can also be described as a polymer fraction with a degree of branching less than 2 methyls/1000 carbons. Among other benefits, the lack of high density polymer fraction permits
15 improved optical properties and enhanced film flexibility.

Such substantially linear ethylene polymers are also characterized by a single DSC melting peak. However, those polymers having a density of about 0.875 g/cm³ to about 0.91 g/cm³, the single melting peak may show, depending on equipment sensitivity, a "shoulder" or a "hump" on it's low
20 melting side that constitutes less than 12 percent, typically, less than 9 percent, and more typically less than of 6 percent of the total heat of fusion of the polymer. This artifact is due to intra-polymer chain variations and is discerned on the basis of the slope of the single melting peak varying monotonically through the melting region of the
25 artifact. Such artifact occurs within 34°C, typically within 27°C, and more typically within 20°C of the melting point of the single melting peak. The single melting peak is determined using a differential scanning calorimeter standardized with indium and deionized water. The method involves about 5-7 mg sample sizes, a "first heat" to about 140°C which is
30 held for 4 minutes, a cool down at 10°/min. to -30°C which is held for 3 minutes, and heat up at 10°C/min. to 140°C for the "second heat". The single melting peak is taken from the "second heat" heat flow vs. temperature curve. Total heat of fusion of the polymer is calculated from the area under the curve. The heat of fusion attributable

to this artifact, if present, can be determined using an analytical balance and weight-percent calculations.

... The substantially linear ethylene polymers are analyzed by gel permeation chromatography (GPC) on a Waters 150 high temperature chromatographic unit equipped with differential refractometer and three columns of mixed porosity. The columns are supplied by Polymer Laboratories and are commonly packed with pore sizes of 10^3 , 10^4 , 10^5 and 10^6 Å. The solvent is 1,2,4-trichlorobenzene, from which 0.3 percent by weight solutions of the samples are prepared for injection. The flow rate is 1.0 milliliters/minute, unit operating temperature is 140°C and the injection size is 100 microliters.

The molecular weight determination with respect to the polymer backbone is deduced by using narrow molecular weight distribution polystyrene standards (from Polymer Laboratories) in conjunction with their elution volumes. The equivalent polyethylene molecular weights are determined by using appropriate Mark-Houwink coefficients for polyethylene and polystyrene (as described by Williams and Ward in Journal of Polymer Science, Polymer Letters, Vol. 6, p. 621, 1968) to derive the following equation:

$$M_{\text{polyethylene}} = a * (M_{\text{polystyrene}})^b.$$

In this equation, $a = 0.4316$ and $b = 1.0$. Weight average molecular weight, M_w , is calculated in the usual manner according to the following formula: $M_w = \sum w_i * M_i$, where w_i and M_i are the weight fraction and molecular weight, respectively, of the i^{th} fraction eluting from the GPC column.

For the substantially linear ethylene interpolymers and homopolymers used in the present invention, the M_w/M_n is preferably less than 3, especially from 1.5 to 2.5.

Single site polymerization catalysts, (for example, the monocyclopentadienyl transition metal olefin polymerization catalysts described by Canich in US Patent 5,026,798 or by Canich in US Patent 5,055,438) or constrained geometry catalysts (for example, as described by Stevens et al. in US Patent 5,064,802) can be used to polymerize the substantially linear interpolymers and copolymers, so long as the catalysts are used consistent with the methods described in USSN 07/776,130 and in USSN

07/939,281. Such polymerization methods are also described in PCT/US 92/08812 (filed October 15, 1992). However, the substantially linear ethylene interpolymers and homopolymers are preferably made by using suitable constrained geometry catalysts, especially constrained geometry catalysts as disclosed in US Application Serial Nos.: 545,403, filed July 3, 1990; 758,654, filed September 12, 1991; 758,660, filed September 12, 1991; and 720,041, filed June 24, 1991.

Suitable cocatalysts for use herein include but are not limited to, for example, polymeric or oligomeric aluminoxanes, especially methyl aluminoxane or modified methyl aluminoxane (made, for example, as described in US Patent 5,041,584, US Patent 4,544,762, US Patent 5,015,749, and/or US Patent 5,041,585) as well as inert, compatible, non-coordinating, ion forming compounds. Preferred cocatalysts are inert, non-coordinating, boron compounds.

The polymerization conditions for manufacturing the substantially linear ethylene homopolymers and interpolymers of the present invention are preferably those useful in the solution polymerization process, although the application of the present invention is not limited thereto. Slurry and gas phase polymerization processes are also useful, provided the proper catalysts and polymerization conditions are employed. To polymerize the substantially linear interpolymers and copolymers useful in the invention, the single site and constrained geometry catalysts mentioned earlier can be used, but the polymerization process should be operated such that the polymers are formed. That is, not all polymerization conditions inherently make the substantially linear ethylene polymers, even when the same catalysts are used.

For example, in one embodiment of a polymerization process useful in making the novel substantially linear ethylene polymers, a continuous process is used, as opposed to a batch process.

Preferably, the polymerization is performed in a continuous solution polymerization process. Generally, manipulation of I_{10}/I_2 while holding M_w/M_n relatively low for producing the substantially linear ethylene polymers using constrained geometry catalyst technology described herein is a function of reactor temperature and/or ethylene concentration. Reduced ethylene concentration and higher temperature generally produces higher I_{10}/I_2 . Generally, as the ethylene concentration of the reactor

decreases, the polymer concentration increases. For the novel substantially linear ethylene interpolymers and homopolymers, the polymer concentration for a continuous solution polymerization process is preferably above 5 weight percent of the reactor contents, especially
5 above 6 weight percent of the reactor contents. Generally, the polymerization temperature of the continuous process, using constrained geometry catalyst technology, is from 20°C to 250°C. If a narrow molecular weight distribution polymer (M_w/M_n of from 1.5 to 2.5) having a higher I_{10}/I_2 ratio (for example, I_{10}/I_2 of 7 or more, preferably at least
10 8, especially at least 9) is desired, the ethylene concentration in the reactor is preferably not more than 8 percent by weight of the reactor contents, especially not more than 6 percent by weight of the reactor contents, and most especially not more than 4 percent by weight of the reactor contents.

15 Multiple reactor polymerization processes can also be used in making the substantially linear olefin interpolymers and homopolymers of the present invention, such as those processes disclosed in US Patent 3,914,342. The multiple reactors can be operated in series or in parallel or a combination thereof, with at least one constrained geometry catalyst
20 employed in at least one of the reactors.

The oriented and unoriented film structures of the present invention can be made using conventional simple hot blown bubble, cast extrusion, or extrusion coating techniques as well as, particularly for oriented films by using more elaborate techniques such as "tenter framing" or the "double
25 bubble" or "trapped bubble" process.

"Stretched" and "oriented" are used in the art and herein interchangeably, although orientation is actually the consequence of a film being stretched by, for example, internal air pressure pushing on the tube or by a tenter frame pulling on the edges of the film.

30 Simple hot blown bubble film processes are described, for example, in The Encyclopedia of Chemical Technology, Kirk-Othmer, Third Edition, John Wiley & Sons, New York, 1981, Vol. 16, pp. 416-417 and Vol. 18, pp. 191-192. Elaborate processes for manufacturing biaxially oriented film such as the "double bubble" process described in US Patent 3,456,044
35 (Pahlke), and other suitable processes for preparing biaxially stretched or oriented film are described in US Patent 4,865,902 (Golike et al.), US

Patent 4,352,849 (Mueller), US Patent 4,820,557 (Warren), US Patent 4,927,708 (Herran et al.), US Patent 4,963,419 (Lustig et al.), and US Patent 4,952,451 (Mueller).

As disclosed by Pahlke in US Patent 3,456,044 and in comparison to the simple bubble method, "double bubble" or "trapped bubble" film processing can significantly increase a film's orientation in both the machine and transverse directions. The increased orientation yields higher free shrinkage values when the film is subsequently heated. Also, Pahlke in US Patent 3,456,044 and Lustig et al. in US Patent 5,059,481 disclose that low density polyethylene and ultra low density polyethylene materials, respectively, exhibit poor machine and transverse shrink properties when fabricated by the simple bubble method, for example, about 3 percent free shrinkage in both directions. However, in contrast to known film materials, and particularly in contrast to those disclosed by Lustig et al. in US Patent 5,059,481; US Patent 4,976,898; and US Patent 4,863,769, as well as in contrast to those disclosed by Smith in US Patent 5,032,463, the unique substantially linear ethylene polymers of the present invention show significantly improved simple bubble shrink characteristics in both the machine and transverse directions. Additionally, when the unique substantially linear ethylene polymers are fabricated by simple bubble method at high blow-up ratios, for example, at greater or equal to 2.5:1, or, more preferably, by the "double bubble" method disclosed by Pahlke in US Patent 3,456,044 and by Lustig et al. in US Patent 4,976,898, it is possible to achieve good machine and transverse direction shrink characteristics making the resultant films suitable for shrink wrap packaging purposes. Blow-Up Ratio, abbreviated herein as "BUR", is calculated by the equation:

$$\text{BUR} = \text{Bubble Diameter} + \text{Die Diameter}.$$

The olefin packaging and wrapping films of the present invention may be monolayer or multilayer films. In those embodiments in which the film structure is a monolayer, the monolayer can comprise at least 10, preferably at least 30 weight percent of at least one substantially linear ethylene polymer, up to 100 weight percent of at least one substantially linear ethylene polymer.

The substantially linear ethylene polymer used to construct the monolayer will depend on the properties desired in the film and in those embodiments in which two or more substantially linear ethylene polymers are used in the construction of the film, these polymers are selected in part based on their compatibility with one another with respect to both processing and use conditions. Similarly, if a blend of one or more substantially linear ethylene polymers and one or more non-substantially linear ethylene polymers (for example conventional, homogeneously branched linear ethylene/ α -olefin copolymers made as described in USP 3,645,992, or conventional, heterogeneously branched ethylene/ α -olefin copolymers made by the Ziegler process as described in USP 4,076,698) are used in the construction of the monolayer, then these non-substantially linear ethylene polymers are selected in part based on their compatibility with the substantially linear ethylene polymer(s).

Depending on their various properties, any of these monolayers can be used in any of the five various packaging methods, but as a practical matter, monolayer films are best adapted for use in the stretch overwrap and skin packaging method. As required for stretch wrapping, monolayer film made from the substantially linear ethylene polymers of the present invention have surprisingly good oxygen permeability. For example, a 2-mil monolayer blown film made from a substantially linear ethylene/1-octene copolymer having 9 percent 1-octene content has an oxygen transmission rate of $720 \text{ cm}^3/\text{mil}/(100 \text{ in}^2/\text{day}/\text{atm})$, which is 15-20 percent greater than the oxygen transmission of a 2-mil monolayer blown film made from a comparative heterogeneously branched LLDPE (also an ethylene/1-octene copolymer having 9 percent 1-octene content) which has an oxygen transmission of $590 \text{ cm}^3/\text{mil}/(100 \text{ in}^2/\text{day}/\text{atm})$. The α -olefin comonomer content in the substantially linear ethylene polymers can be determined by infrared techniques, (ASTM D-2238 Method B).

Oxygen transmission is particularly beneficial in stretch wrap packaging of individual cuts of red meat (that is, "in-store" wrapped meat where the grocer/butcher actually cuts the primal meat into smaller cuts for individual sale), where oxygen permeability allows fresh red meat to "bloom" to the desired bright red color. Film useful in packaging individual cuts of red meat will usually have minimal shrinkage and good stretchability. The film preferably is oxygen permeable and has good

elastic recovery, to enable the consumer to examine the meat without permanently deforming the film and making it unattractive. Co-pending US application entitled "Method of Packaging Food Products", filed of April 28, 1993 in the names of Pak-Wing Steve Chum and Nicole F. Whiteman, 5 discloses methods of wrapping food articles, including such individual portions of red meat. The film used in packaging individual portions of red meat, could, however, be prepared as a heat-shrinkable film, even though current technology does not utilize shrink characteristics.

One particularly desirable monolayer for use in the stretch overwrap 10 method is a blend of substantially linear olefin polymer and an ethylene/ α,β -unsaturated carbonyl copolymer such as EVA, EAA, ethylene/methacrylic acid (EMAA), and their alkali metal salts (ionomers), esters and other derivatives.

For coextruded or laminated multilayer film structures (for example, 15 3 and 5-layer film structures), the substantially linear ethylene polymer described herein can be used as a core layer, an outer surface layer, an intermediate layer and/or a inner sealant layer of the structure. In particular, for the hot tack film of the present invention, at least one of the novel substantially linear ethylene/ α -olefin copolymers described 20 herein is used as at least one heat sealable outer layer of the film structure. The heat sealable outer layer can be coextruded with the other layer(s) or the heat sealable outer layer can be laminated onto another layer(s) in a secondary operation, such as that described in Packaging Foods With Plastics, by Wilmer A. Jenkins and James P. Harrington (1991) or that described in "Coextrusion For Barrier Packaging" by W.J. Schrenk and C.R. Finch, Society of Plastics Engineers RETEC Proceedings, June 15- 25 17 (1981), pp. 211-229.

Generally for a multilayer film structure, the substantially linear ethylene interpolymers or homopolymers described herein comprise at least 30 10 percent of the total multilayer film structure. Other layers of the multilayer structure include but are not limited to barrier layers, and/or tie layers, and/or structural layers. Various materials can be used for these layers, with some of them being used as more than one layer in the same film structure. Some of these materials include: foil, nylon, 35 ethylene/vinyl alcohol (EVOH) copolymers, polyvinylidene chloride (PVDC), polyethylene terephthalate (PET), oriented polypropylene (OPP),

ethylene/vinyl acetate (EVA) copolymers, ethylene/acrylic acid (EAA) copolymers, ethylene/methacrylic acid (EMAA) copolymers, ULDPE, LLDPE, HDPE, MDPE, LMDPE, LDPE, ionomers, graft-modified polymers (for example, maleic anhydride grafted polyethylene), and paper. Generally, the
5 multilayer film structures comprise from 2 to 7 layers.

In one embodiment disclosed herein, a multilayer film structure comprising at least three layers (for example, an "A/B/A" structure), wherein each outer layer comprises at least one substantially linear ethylene polymer, and at least one core or hidden layer is a high pressure
10 branched low density polyethylene (LDPE). This multilayer film structure shows surprisingly good optical properties, while maintaining good overall film strength properties. Generally, the ratio of the film structure layers is such that the core layer dominates the film structure in terms of its percentage of the entire structure. The core layer should be at
15 least 33 percent of the total film structure (for example, in a three layer film structure, each "A" outer layer comprises 33 percent by weight of the total film structure, while the core LDPE layer (the "B" layer) comprises 33 percent by weight of the total film structure). In a three
20 layer film structure, preferably, the core LDPE layer comprises at least 70 percent of the total film structure. Additional hidden layers can also be incorporated into the film structures without detriment to the optical properties. For example, tie or intermediate layers comprising, for
example, ethylene/vinyl acetate copolymers, ethylene acrylic acid copolymers or anhydride graft-modified polyethylenes can be used, or
25 barrier layers comprising, for example, vinylidene chloride/vinyl chloride copolymers or ethylene vinyl alcohol copolymers can be used. In a more preferred three layer film structure, each "A" outer layer comprises 15 percent by weight of the total film structure of at least one
substantially linear ethylene polymer, and the "B" core layer comprises 70
30 percent by weight of the total film structure of LDPE. The multilayer film structure can be oriented and/or irradiated (in any order) to provide a multilayer shrink film structure or a skin package with controlled linear tearability. For the multilayer film structures disclosed herein having improved optical clarity, the LDPE generally has a density from
35 0.915 g/cm³ to 0.935 g/cm³; a melt index (I₂) from 0.1 g/10 minutes to 10 g/10 minutes; and a melt tension of at least 1 gram. For improved

optical clarity, the substantially linear ethylene/ α -olefin polymer generally has a density from 0.85 g/cm³ to 0.96 g/cm³, preferably from 0.9 g/cm³ to 0.92 g/cm³; a melt index (I₂) from 0.2 g/10 minutes to 10 g/10 minutes, preferably from 0.5 g/10 minutes to 2 g/10 minutes; a molecular weight distribution (M_w/M_n) not greater than 3; and a single melting peak as determined using DSC.

The multilayer film structures can also be oxygen permeable either by using the substantially linear ethylene polymers (SLEP) alone in the film, or in combination with other oxygen permeable film layers such as, for example, ethylene/vinyl acetate (EVA) and/or ethylene/acrylic acid (EAA). Of particular interest, for example, are SLEP/EAA/SLEP, SLEP/VLDPE/SLEP and LLDPE/SLEP/LLDPE film structures which are replacements for conventional films such as PVC and are well suited for stretch overwrapping various fresh foods, for example retail-cut red meats, fish, poultry, vegetables, fruits, cheeses, and other food products destined for retail display and that benefit from access to environmental oxygen or must appropriately respire. These films are preferably prepared as nonshrink films (for example, without biaxial orientation induced by double bubble processing) with good oxygen permeability, stretchability, elastic recovery and heat seal characteristics, and can be made available to wholesalers and retailers in any conventional form, for example stock rolls, as well as be used on conventional packaging equipment.

In another aspect, the multilayer film structures can comprise an oxygen barrier film (for example, SARAN[®], a film made from a polyvinylidene chloride polymer made by The Dow Chemical Company, or EVAL[®] resins which are ethylene/vinyl alcohol copolymers made by Eval Company of America, a division of Kuraray of America, Inc., a wholly owned subsidiary of Kuraray Ltd.). Oxygen barrier properties are important in film applications such as packaging primal cuts of meat (that is, large cuts of meat which are shipped to a specific store for further cutting for specific consumer consumption). As described by Davis et al. in US Patent 4,886,690, the oxygen barrier layer can also be designed as "peelable" to allow removal once the packaged primal cut arrives at the butcher/grocer; a peelable construction or design is particularly useful for "case-ready" vacuum skin packages of individual portions and eliminates the need for repackaging to an oxygen permeable package for blooming to bright red.

The film structures made with both the substantially linear ethylene homopolymers and interpolymers described herein may also be pre-formed by any known method, such as, for example, by extrusion thermoforming, with respect to the shape and contours of the product to be packaged. The benefit of employing pre-formed film structures will be to complement or avoid a given particular of a packaging operation such as augment drawability, reduced film thickness for given draw requirement, reduced heat up and cycle time, etc.

The thickness of the monolayer or multilayer film structures may vary. However, for both the monolayer and multilayer film structures described herein, the thickness is typically from 0.1 mils (2.5 micrometers) to 50 mils (1270 micrometers), preferably from 0.4 mils (10 micrometers) to 15 mils (381 micrometers), and especially from 0.6 mils (15 micrometers) to 4 mils (102 micrometers).

Film structures made from both the substantially linear ethylene interpolymers and homopolymers described herein will show surprisingly more efficient irradiation crosslinking as compared to a comparative conventional Ziegler polymerized linear ethylene/ α -olefin polymer. As one aspect of this invention, by taking advantage of the irradiation efficiency of these unique polymers, it is possible to prepare film structures with differentially or selectively crosslinked film layers. To take further advantage of this discovery, specific film layer materials including the present substantially linear ethylene polymers can be formulated with pro-rad agents, such as triallyl cyanurate as described by Warren in US Patent 4,957,790, and/or with antioxidant crosslink inhibitors, such as butylated hydroxytoluene as described by Evert et al. in US Patent 5,055,328.

Irradiation crosslinking is also useful for increasing the shrink temperature range and the heat seal range for the film structures. For example, US Patent 5,089,321 discloses multilayer film structures comprising at least one heat sealable outer layer and at least one core layer which have good irradiation cross-linking performance. Among irradiation crosslinking technologies, beta irradiation by electron beam sources and gamma irradiation by a radioactive element such as Cobalt 60 are the most common methods of crosslinking film materials.

In an irradiation crosslinking process, a thermoplastic film is fabricated by a blown film process and then exposed to an irradiation source (beta or gamma) at an irradiation dose of up to 20 Mrad to crosslink the polymeric film. Irradiation crosslinking can be induced
5 before or after final film orientation whenever oriented films are desired such as for shrink and skin packaging, however, preferably irradiation crosslinking is induced before final orientation. When heat-shrinkable and skin packaging films are prepared by a process where pellet or film irradiation precedes final film orientation, the films invariably show
10 higher shrink tension and will tend to yield higher package warpage and board curl; conversely, when orientation precedes irradiation, the resultant films will show lower shrink tension. Unlike shrink tension, the free shrink properties of the substantially linear ethylene polymers of the present invention are essentially unaffected by whether irradiation
15 precedes or follows final film orientation.

Irradiation techniques useful for treating the film structures described herein include techniques known to those skilled in the art. Preferably, the irradiation is accomplished by using an electron beam (beta) irradiation device at a dosage level of from 0.5 megarad (Mrad) to
20 20 Mrad. Shrink film structures fabricated from the substantially linear polymers as described herein are also expected to exhibit improved physical properties due to a lower degree of chain scission occurring as a consequence of the irradiation treatment.

As oriented or unoriented, monolayer or multilayer structures, the
25 hot tack films of the present invention have utility in bag-n-box and form-fill-seal operations. An example of the use of the films of the present invention in form-fill-seal operations is described in Packaging Foods With Plastics, by Wilmer A. Jenkins and James P. Harrington (1991), pp. 32-83. Packages can also be formed by vertical or horizontal
30 form/fill/seal packaging and thermoform/fill/seal packaging, as described in "Packaging Machinery Operations: No. 8, Form-Fill-Sealing, A Self-Instructional Course" by C. G. Davis, Packaging Machinery Manufacturers Institute (April 1982); "The Wiley Encyclopedia of Packaging Technology" by M. Bakker (Editor), John Wiley & Sons (1986) (pp. 334, 364-369); and
35 "Packaging: An Introduction" by S. Sacharow and A. L. Brody, Harcourt Brace Javanovich Publications, Inc. (1987) (pp. 322-326). A particularly

useful device for form/fill/seal operations is the Hayssen Ultima Super CMB.Vertical Form/Fill/Seal Machine, which packages typical products such as food, pharmaceuticals and hardware. Other manufacturers of pouch thermoforming and evacuating equipment include Cryovac and Koch.

- 5 The olefin packaging and wrapping films of this invention, and the methods for preparing them, are more fully described in the following examples. The substantially linear ethylene polymers used in the following examples were prepared as described in the Examples of US Patent Applications USSN 07/776,130 and USSN 07/939,281.

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EXAMPLES

TABLE 1

Physical Properties of Biaxially Oriented
Simple Bubble Monolayer Films*

Film	Resin Type	Density (g/cc)	Melt Index** (g/10 min.)	I ₁₀ /I ₂ Ratio	PI (kpoise)	1% Secant Modulus, kPa	Tensile Strength, MPa	Toughness (kJ/m ²)	Puncture (Kg-cm/ml)
A	ULDPE	0.912	1.0	8.2	13.6	145,168	38.6	1,172	4.9
B	SLEP	0.915	1.0	10.4	8.2	156,836	47.6	1,559	5.6
C	SLEP	0.912	1.0	10.2	9.3	136,462	46.8	1,391	5.7
D	SLEP	0.902	1.0	8.8	4.1	79,137	57.7	1,260	6.9

*All films fabricated at a 2.5:1 BUR, except Film D which was fabricated at a 3.0:1 BUR. ULDPE denotes ultra low density polyethylene and SLEP denotes substantially linear ethylene polymer.

**Melt Index values at ± 0.1 g/10 minutes.

- 15 Samples A - K were all simple bubble blown films. Samples A, E and F were comparative samples only and were not examples of the invention. To prepare the films, resin samples were extruded on a 2.5 inch (6.35 cm) diameter Gloucester extruder equipped with a 6 inch (15.2 cm) annular die. Output rate was targeted at 120 or 150 lbs/hr. (54.5 or 68.2 kg/hr.) and
20 melt temperature was targeted at 440 F (227°C). Film blow-up ratio (BUR)

was varied at 2.5:1, 3.0:1 and 3.5:1 and films were prepared at 1 and 2 mils. Film tensile and toughness properties were obtained in accordance to ASTM D-882, Procedure A where toughness was taken as the integration of the area under the stress-strain curve. 1 percent Secant Modulus values
5 were obtained in accordance with ASTM D-638. The Secant Modulus, tensile strength and toughness data are all reported as the average of machine and transverse direction single determinations for each respective film.

The puncture values were obtained using an Instron tensiometer. A hemispherical 12.5 mm diameter aluminum probe was used at 250 mm/min.
10 deformation rate to exaggerate ordinary abuse.

The ULDPE film material was prepared from a commercial ethylene/1-octene linear copolymer polymerized using a conventional Ziegler catalyst and is sold by The Dow Chemical Company under the tradename of ATTANE® 4201. All of the substantially linear ethylene polymers in Table 1 are
15 ethylene/1-octene interpolymers polymerized from novel constrained geometry catalyst.

All films made from novel substantially linear ethylene polymers exhibited improved toughness, tensile strength and puncture resistance properties that are highly desired for heat-shrink, stretch wrap, form-
20 fill-seal, vacuum form and skin packaging of food, beverages and nonfood items.

Free shrink properties of the films were determined by cutting four inch by four inch (10.2 cm x 10.2 cm) samples from each of the fabricated film samples and carefully placing them flat into the bottom of silicone-
25 coated metal pans. The metal pans had sides 1 inch (2.5 cm) high and were well-coated with 200 centipoise silicone oil. The pans containing the film samples were then placed into a forced-air convection oven at 135°C. for ten minutes. After ten minutes, the pans were removed from the oven and allowed to cool to ambient (about 23°C). After cooling, the film
30 samples were removed and the dimensions in both the machine and transverse directions were measured. The percent free shrinkage was determined as described in ASTM D-2732.

Table 2 shows the novel substantially linear ethylene polymers exhibited excellent heat-shrink characteristics making them suitable as
35 shrink films and bags for food and nonfood items such as papergoods.

TABLE 2

Free Shrinkage of Biaxially Oriented
Simple Bubble Monolayer Films

Film	Resin Type	Density (g/cc)	Melt Index, 190°C** (g/10 min.)	Thickness (Mils)	Blow Up Ratio	Percent Free Shrinkage	
						Machine Direction	Transverse Direction
A	ULDPE*	0.912	1.0	2.0	2.5:1	65	-22
E	ULDPE	0.912	1.0	1.0	3.5:1	75	0
F	LLDPE	0.920	1.0	1.0	3.0:1	74	-8
D	SLEP	0.902	1.0	2.0	2.5:1	75	3
G	SLEP	0.902	1.0	1.0	3.0:1	80	13
H	SLEP	0.902	1.0	1.0	3.5:1	80	30
I	SLEP	0.911	1.0	1.0	3.5:1	79	28
J	SLEP	0.920	1.0	1.0	3.0:1	79	11
K	SLEP	0.920	1.0	1.0	3.5:1	79	26

* ULDPE denotes ultra low density polyethylene, LLDPE denotes linear low density polyethylene and SLEP denotes substantially linear ethylene polymer.

**Melt Index values at ± 0.1 g/10 minutes.

Table 3 lists the samples used in the following packaging film examples. Comparative polymer samples 1 and 2 were heterogeneously branched linear low density polyethylene (LLDPE) polymers produced by a conventional high efficiency Ziegler type catalyst. Comparative sample 5 was a low density polyethylene (LDPE) produced under high pressure/free radical polymerization. Samples 3 and 4 were substantially linear ethylene interpolymers produced using a constrained geometry catalyst. Comparative sample 6 was a commercially available high clarity shrink film, Clysar™ XEH 921, sold by E. I. du Pont de Nemours Company.

Table 4 lists the critical shear stress at onset of gross melt fracture for comparative examples 1 and 2 and for examples 3 and 4. The

critical shear stress was greater than 18 percent higher for substantially linear ethylene interpolymers produced using a constrained geometry catalyst, which was indicative of less susceptibility to gross melt fracture.

5

Table 3

Samples For Shrink Film Performance Comparison

Sample	Polymer	Density (g/cm ³)	I ₂ (g/10 min)	I ₁₀ /I ₂	M _w /M _n	Catalyst	DSC Melting Point** (°C)
1*	Ethylene/ 1-octene	0.92	1	8.5	3.8	Ziegler	121
2*	Ethylene/ 1-octene	0.902	0.98	8.3	3.57	Ziegler	121
3	Ethylene/ 1-octene	0.902	0.93	8.8	2.1	Constrained geometry	95
4	Ethylene/ 1-octene	0.902	1.03	8.5	2.09	Constrained geometry	95
5*	LDPE	0.923	1.9	NM	NM	High pressure/free radical	110
6*	Clysar TM XEH 921***	NM	NM	NM	NM	NM	121

*Comparative Sample Only; not an example of the invention

**Second heat, 10°C/min.

***Biaxially Oriented Crosslinked Film Sample, 1.5 mils thickness

NM = Not Measured

10

Table 4

Sample	Critical shear stress at OGMF** (dynes/cm ²)
1*	3.64 x 10 ⁶
2*	3.42 x 10 ⁶
3	4.31 x 10 ⁶
4	4.31 x 10 ⁶

*Comparative Sample Only; not an example of this invention

**Onset of gross melt fracture

15

Samples 1, 2, and 4 were simple bubble hot blown film fabricated on a 2.5 inch (6.4 cm) diameter Gloucester extruder equipped with a 6 inch (15.2 cm) annular die. A target output rate of 150 lbs/hr. (68 kg/hr), 440 F (227°C) target melt temperature and 3:1 blow up ratio were used

20

resulting in a film thickness of about 1 mil. The optical properties were measured as described in ASTM D-1746, D-1003, and D-2457.

Table 5 compares the optical properties, that is, clarity, gloss, and percent film haze as well as the free shrink characteristics of films made from substantially linear ethylene interpolymers versus films made from ethylene/ α -olefin copolymers made using a Ziegler catalyst. Whereas the inventive Sample 4 exhibited transverse directional (TD) shrink, a desirable shrink film property, comparative samples 1 and 2 exhibit undesirable TD expansion. Furthermore, the film fabricated from the inventive Sample 4 exhibited superior overall optical properties (as measured by higher 20° gloss and lower percent haze) relative to comparative samples 1 and 2.

Table 5

Sample	Clarity (percent Transmission)	20° Gloss	Haze (percent)	Free Shrink at 135°C (percent) MD	Free Shrink at 135°C (percent) TD
1*	72.8	93.5	5.2	73.8	-7.9
2*	28.5	85.7	3.6	71.0	-9.9
4	73.2	125	1.2	80.2	9.4

*Comparative sample only; not an example of the invention

Example 3

Sample 3 and comparative sample 5 were processed as described in Example 2, except the target melt temperature was 390°F (224°C) and the target blow-up ratio (BUR) was 3.5:1. The resultant 1.0 mil thick film samples were compared with comparative sample 6 with respect to percent film haze, tensile properties, free shrink and shrink tension. The shrink tensions were measured at the DSC melting point (shown in Table 3) of the polymers, since tension measurement at respective melting points are known to yield the most severe film shrink tension.

Table 6

Sample	20° Gloss	Haze (percent)	Ult. Tensile lb/in ² (MPa) MD	Ult. Tensile lb/in ² (MPa) TD	Free Shrink (percent) MD	Free Shrink (percent) TD	Shrink Tension* (g/in) (g/cm) MD	Shrink Tension* (g/in) (g/cm) TD
3	107	2.7	9,367 (64.5)	8616 (59.4)	79.8	30.3	12 (4.7)	< 3*** (<1.2)
5**	66	6.0	3,584 (24.7)	3332 (23.0)	81	29	15 (5.9)	< 3*** (<1.2)
6**	117	3.5	14,151 (97.5)	13049 (89.9)	72	71	168 (66.1)	> 200 (78.7)

*Measured at the DSC melting point of the polymer sample

**Comparative sample only; not an example of this invention

5 ***Values are too low to be accurately determined using the 200 gm load cell

As shown in Table 6, comparative sample 5 exhibited adequate free shrink properties, yet its optical and tensile properties did not meet the desired performance levels for industrial (transit) or retail packaging.

10 Comparative sample 6 exhibited superior optical, free shrink and tensile properties, however for shrink or skin packaging of delicate or warp sensitive goods, the high shrink tension exhibited by this film was excessive. The Inventive Sample 3 exhibited an excellent combination of superior optics, good tensile properties, good free shrink and low shrink
15 tension.

Comparative Example 4

A blend of 75 percent by weight (based on the final blend) of an ethylene/1-octene copolymer having a melt index (I₂) of about 1 g/10
20 minutes and a density of about 0.92 g/cm³ produced by Ziegler catalysis and 25 percent (by weight of the final blend) of a LDPE having a melt index (I₂) of about 1.9 g/10 minutes and a density of about 0.923 g/cm³ produced by a high pressure/free radical polymerization process was fabricated into film on a 2.5 inch (6.4 cm) diameter Gloucester film line
25 at a blow-up ratio (BUR) of 3:1, a melt temperature of 227°C, a die gap of 70 mils and a film thickness of about 1 mil. The percent free shrink properties were measured at 135°C in both the machine (MD) and transverse (TD) directions as described earlier. The film had MD shrink of about 74.8 percent and TD shrink of about -9.4 percent, thereby demonstrating

that this film, which employs LDPE for enhanced shrink characteristics, actually showed undesirable TD expansion.

Example 5 and Comparative Example 6

5 Example 5 was a substantially linear ethylene/1-octene copolymer having a density of 0.900 g/cm³, a melt index (I₂) of about 0.8 g/10 minutes, a molecular weight distribution (M_w/M_n) of about 2.2, and a melt flow ratio (I₁₀/I₂) of about 8.5. Comparative Example 6 was a
10 heterogeneously branched LLDPE ethylene/1-octene copolymer having a density of 0.905 g/cm³, a melt index (I₂) of about 0.8, a molecular weight distribution (M_w/M_n) of about 3.5 and a melt flow ratio (I₁₀/I₂) of about 8. Sample pellets of these copolymer examples were exposed to electron beam radiation at E beam Services, Inc. (Canterbury, NJ) and tested for cross-link density as measured by percent gel in xylene in accordance with
15 ASTM D-2765 and as described by Chum et al. in US Patent 5,089,321. Table 7 summarizes the data:

Table 7

Radiation Exposure (Mrad)	Example 5 (percent gel)	Comparative Example 6 (percent gel)
0	0	0
5.0	58	49

20 As the data in Table 7 demonstrate, a higher cross-link density was achieved more efficiently for irradiated substantially linear ethylene polymer pellets (Inventive Example 5) relative to pellets of a heterogeneously branched LLDPE having a comparable density, melt index and melt flow ratio.

25

Inventive Examples 7 and 8, and Comparative Examples 9 and 10

In another experiment, samples of sheeting (18.5 ± 1.5 mil thick) of the same substantially linear copolymer as was mentioned in Example 5 was irradiated at E Beam Services, Inc. at a dosage of 0 and 2.5 Mrad and
30 subsequently biaxially stretched using a T.M. Long laboratory biaxial stretching (tenter) frame. The stretching temperature utilized was a

temperature below the DSC melting point of the copolymer but 5°C above the temperature at which tearing of the sheet occurs during stretching. These samples are described as Examples 7 and 8, respectively, for 0 and 2.5 Mrad dosage. Samples of sheeting (18.5 ± 1.5 mil thick) of the same linear heterogeneous copolymer as described in comparative example 5 were also irradiated at 0 and 2.5 Mrad and subsequently biaxially stretched with the laboratory stretching frame as described above. These samples are described as comparative examples 9 and 10, respectively. Clear, low haze films resulted after irradiation that were tested for free shrink at 95°C as described in Example 1. Table 8 summarizes the data as well as provides information indicating how the films were uniformly stretched using the T.M. Long stretching frame:

Table 8

15

Sample	Stretching Temperature* (°C)	Stretch Ratio	Free Shrink (percent) MD	Free Shrink (percent) TD
Inventive Example 7	88	3 x 3	> 35	> 35
Inventive Example 8	88	4 x 4	> 35	> 35
Comparative Example 9	97	4 x 4	< 25	< 25
Comparative Example 10	97	4 x 4	< 25	< 25

The data in Table 8 show that the sheets fabricated from a substantially linear ethylene polymer exhibited superior shrink performance over comparable sheets fabricated from a conventional, heterogeneous linear ethylene polymer. The superior shrink performance was exhibited even when the amount of biaxial stretching was significantly lower for the Inventive Examples relative to the comparative examples. The Inventive Example showed superior free shrink performance regardless of whether the comparative examples were irradiated or not prior to orientation (stretching).

Inventive Example 11 and Comparative Example 12:

Three layer film structures were made using different ethylene polymers in each layer. The film structures were made on a hot blown bubble coextrusion film line. Layer "A" was extruded using a 2.5 inch (6.4 cm) diameter Egan extruder equipped with a single flighted screw having two Egan-type mixing sections. Layer "B" was extruded using a 2.5 inch (6.4) diameter Egan extruder equipped with a single flighted screw having two Maddock type mixing sections. Layer "C" was extruded using a 2 inch (5.1 cm) diameter Egan extruder equipped with a single flighted screw having one Maddock type mixing section. The total configuration was set for a target output of about 150 pounds/hour. The weight output ratio of the extruders was targeted at 15 percent/70 percent/15 percent for the A/B/C extruders. Polymer melt temperatures were targeted at 415°F/450°F/425°F (239°C/261°C/246°C) for layers A/B/C, respectively. A 70 mil die gap was used for the eight inch (20.3 cm) die. The films were blown to a 3.5:1 blow-up ratio (BUR) to produce 1.25 mil thick multilayer films. Frost line height was about 20 inches (51 cm). Gloss, haze, and clarity tested in accordance with ASTM D-1746, ASTM D-1003, and ASTM D-2457, respectively. Table 9 summarizes the physical properties of the polymers used in the various layers:

Table 9

Polymer	Polymer Type	Melt Index (g/10 min.)	Density (g/cm ³)	I ₁₀ /I ₂	M _w /M _n
1	LDPE	0.7	0.9235	NM	NM
2	Substantially Linear Ethylene 1-Octene Copolymer	1.0	0.9	8.95	2.15

NM = Not Measured

The multilayer film structures and their respective optical properties are identified in Table 10:

Table 10

Example	Polymers used in the Film Structure (A/B/A)	20° Gloss	Haze (percent)
11	2/1/2	111.6	2.7
12*	1/1/1	34.5	10.1

*Comparative Example Only; not an example of this invention

- 5 As the data in Table 10 show, multilayer film structures made using the substantially linear ethylene/ α -olefin polymer as the outer layer of the film, with LDPE used as a core or hidden layer, had surprisingly good optical properties versus a multilayer film structure made using the LDPE alone as all three layers. Thus, by coextruding thin outer layers of a
- 10 substantially linear ethylene polymer onto a LDPE core layer, the resultant film structure exhibited highly favorable optical properties.

Inventive Example 13 and Comparative Examples 14-19:

- In another experiment, four commercially available meat wrap films
- 15 were obtained and simple bubble hot blown films (1 mil thick) from one representative substantially linear ethylene/1-octene copolymer and two conventional, heterogeneous linear ethylene/1-octene copolymers were prepared on an extrusion line equipped with a 3 inch (7.6 cm) die and a 2 inch (5.1 cm) diameter screw at conditions similar to those described in
- 20 Example 3 of USP 5,089,321 and at a blow-up ratio (BUR) of 2.5:1. The descriptions of the substantially linear ethylene copolymer and the two conventional ethylene copolymers are provided in Table 11 and the descriptions of the commercial meat wrap films are provided in Table 12.

Table 11

Example	Density (g/cm ³)	Melt Index (g/10 min.)	I ₁₀ /I ₂	M _w /M _n
13 [†]	0.902	1.0	7.25	2.2
14*	0.905	0.8	8.7	5.0
15*	0.900	1.0	9.2	5.2

[†]Substantially Linear ethylene/1-octene copolymer; an inventive example.

*Conventional linear ethylene/1-octene copolymer; comparative example and not an example of this invention.

5

Table 12

Example	Film Type	Supplier
16*	PVC	Borden Inc.
17*	EVA-based	Mitsubishi Petrochemical Co. of Japan; trademark YUKA WRAP
18*	EVA-based	Asahi Chemical Co. of Japan; trademark SUNTEC C-100.
19*	EVA/EP elastomer	Asahi Chemical Co. of Japan; trademark SUNTEC C-400.

10

The elastic recovery of the seven films were determined by the Tensile Hysteresis Test in accordance with ASTM D-412. The test procedure is as follows:

- 15 1. Mount a 1" (2.54 cm) wide, 0.5 to 1 mil thick film on an Instron with a gauge length set for 2 inches (5.1 cm).
- 20 2. Stretch the film on the Instron to 25 percent elongation, then allow the film to snap back by returning the Instron crosshead to its original position until the load cell reads zero.
3. Measure the unrecoverable strain and calculate the percent film recovery at 25 percent film elongation.

4. Repeat the experiment at 50 percent film elongation to measure the percent film recovery at 50 percent film elongation.

5 The percent recovery data for Inventive Example 13 and comparative examples 14-19 are shown in Table 13. The data clearly show that the film made from the substantially linear ethylene polymer was well suited for stretch wrap packaging applications due to its excellent elastic recovery relative to conventional LLDPE films and commercial meat wrap films at both 50 percent and 25 percent
10 elongation.

Table 13

Example	Elastic Recovery at 50 percent Elongation	Elastic Recovery at 25 percent Elongation
13	88	91
14*	74	NM
15*	80	82
16*	77	82
17*	82	88
18*	76	86
19*	60	78

15 *Comparative Example; not an example of this invention
NM = not measured

Inventive Example 20 and Comparative Examples 21-23:

In another experiment, 5 mil film was fabricated from one
20 substantially linear ethylene polymer, two conventional heterogeneous linear ethylene polymers and a Surlyn® ionomer supplied by E.I. du Pont. The physical properties, including film optics and abuse or implosion resistance properties such as ultimate tensile strength and toughness, of the resultant films are shown in Table 14:

Table 14

Example	Polymer	I ₂ (g/10 min)	Density (g/cm ³)	Vicat Softening (°C)	Ultimate Tensile (MPa)	Toughness (kJ/m ²)	20 Degree Gloss
ASTM Test Method		D 1238 190°C 2.16 kg	D 792	D 1525	D 882	D 822	D 2457
20	SLEP	1.0	0.908	94.3	51.4	3,249	119.2
21*	ULDPE	1.0	0.912	95.3	40.0	2,765	55.9
22*	ULDPE	0.8	0.905	82.5	31.4	2,040	55.3
23*	Ionomer	1.3	NM	76.5	36.3	2,219	84.6

*Comparative Example; not an example of this invention

5

The films listed in Table 14 were also used in a skin packaging evaluation using an Ampak Shipmate II skin packaging machine and porous 24 point solid bleached sulfate (SBS) paperboard primed with an ionomer aqueous dispersion. While pre-heat times were varied in the

10 evaluation, heat time was 5 seconds, cool time was 5 seconds, stand-by heater was at 15 percent and packaging vacuum was at 80 percent. Comparative determinations were made for cycle time, board adhesion and vacuum forming (drawability). For various films, cycle time (time to

15 double droop, or time the film is molten enough to begin a packaging cycle) was determined at 21 and 23 second pre-heat times. The adhesion of the films to the paperboard was determined at several pre-heat times by pulling the film from the paperboard with an Instron tensiometer using a 20 kg load setting and a crosshead speed of 25 cm/min. Adhesion testing was performed at least 24 hrs. after blank packages

20 were prepared. For the adhesion test, the samples were cut into four 1 x 5 inch (2.5 cm x 12.7 cm) strips. After a section of the film was peeled from the board, the board was bent 90 degrees and placed in the lower jaw and the film in the upper jaw of the Instron. Adhesion observation and/or measurements were taken once a 180 degree peel

25 began. Drawability was assessed by packaging two 3 inch x 2.5 inch outside diameter, O.D., (7.6 cm x 6.4 cm O.D.) PVC pipes separated 6 inches (15.2 cm) on the board and standing upright, taking observation regarding package tightness, whether a hole developed at the center of

a pipe, as well as by quantifying ridges for each pipe and/or bridge height between the two pipes that developed. Ridges typically occur around the base of a pipe and are manifested as wrinkles. Bridging occurs due to incomplete drawdown to the board. Table 15 summarizes the skin packaging results.

Table 15

Example	Cycle Time at 23 sec Pre-Heat (sec)	Cycle Time at 21 sec Pre-Heat (sec)	Board Adhesion at 13 sec Pre-Heat (kg/cm)	Board Adhesion at 23 sec Pre-Heat (kg/cm)	Ridge Count for Packaged PVC Pipe (number)	Bridge Height for Packaged PVC Pipe (cm)
20	18	17	FT	FT	8	0.3
21*	NM	19	FT	NM	13	0.3
22*	NM	18	FT	NM	10	0.5
23*	18	16	FT	0.19	11	0.3

NM = not measured

FT = fiber tear which is the desired level of excellent, inseparable adhesion

*Comparative Example; not an example of this invention

The data in Table 15 show that skin packaging cycle time of the film made from the substantially linear ethylene polymer was surprisingly equivalent to the Surlyn® ionomer film and the lower density conventional linear ethylene polymer, even though both comparative film material possessed significantly lower Vicat softening points and the ionomer is known to have more infra-red heat bands than nonpolar ethylene polymers. Also, surprisingly, the unique substantially linear ethylene polymer film exhibited better board adhesion at higher pre-heat temperatures than the ionomer film. This performance was particularly surprising since the SBS board was primed with an ionomer aqueous dispersion and was advertised for sale as "primed/coated for Surlyn®". This result was even more surprising given the nonpolar nature of the substantially linear ethylene polymer and the known tendency for nonpolar polymers to exhibit poor adhesion to polar substrates such as the Surlyn® dispersion coating. In addition to unexpected cycle time and adhesion performance, Table 15 also shows the substantially linear ethylene polymer film exhibited better drawability or formability than the ionomer film and films made from

conventional linear ethylene polymers as exemplified by less packaging defects or wrinkles.

Table 16

Samples For Hot Tack Film Performance Comparison

Example	Polymer	Density (g/cm ³)	I ₂ (g/10 min)	I ₁₀ /I ₂	M _w /M _n	DSC melt. point** (°C)
24	Ethylene/ 1-octene	0.87	1	7.5	1.9	55
25*	Elvax® 3165 (ethylene/ vinyl acetate)	18 percent VA	0.7	NM	NM	86
26	Ethylene/ 1-octene	0.902	1	8.8	2.2	95
27	Ethylene/ 1-octene	0.91	1	9.3	2.2	103
28*	Surlyn® 1601 (ionomer)	NM	1.3	NM	NM	94
29*	PRIMACOR® 1410 (ethylene/ acrylic acid)	9.7 percent AA	1.5	NM	NM	96
30*	Ethylene/ 1-octene	0.902	1	9.5	4.1	MMP [†]
31*	Ethylene/ 1-octene	0.912	1	8.6	3.7	MMP [†]
32	Ethylene/ 1-octene	0.9	1	8.8	2.2	95
33*	Tafmer® A 4085 (ethylene/ 1-butene)	0.886	4	5.5	1.9	78

5 *Comparative Example Only; not an example of the invention

**Second heat, 10°C/min

NM = Not Measured

[†]MMP = Not Measured, but has multiple melting peaks

10 In another evaluation, three layer blown coextruded films were made using nylon, an adhesive layer, and a sealant layer. The coextruded films were made using a coextrusion blown film line manufactured by Egan Machinery equipped with two 24:1 L/D 2.5 inch (6.4 cm) extruders and one 24:1 L/D 2 inch (5.1 cm) extruder, and an 8 inch (20.3 cm) spiral mandrel die. The nylon layer was about 1 mil thick, the adhesive layer was about 0.5 mils thick and the sealant layer was about 1.5 mils thick.

The adhesive layer was a blend of maleic anhydride grafted high density polyethylene (HDPE) and linear low density polyethylene (LLDPE). The blend comprised about 10 weight percent HDPE (ethylene homopolymer)

having a melt index of about 10 g/10 minutes and a density of about 0.962 g/cm³ grafted with about 1 percent (final HDPE weight basis) of maleic anhydride blended with a balance of LLDPE (ethylene/1-octene copolymer) having a melt index of about 2.3 g/10 minutes and a density of about 0.917 g/cm³. The nylon was a 6/6,6 copolymer manufactured by BASF under the tradename Ultramid® C-35.

The sealant layers included: Surlyn® 1601 ionomer (a sodium ionomer having I₂ of 1.3 g/10 minutes made by E. I. DuPont de Nemours from an ethylene methacrylic acid (EMAA) copolymer; PRIMACOR® 1410 adhesive resin (an ethylene acrylic acid copolymer made by The Dow Chemical Company having I₂ of 1.5 g/10 minutes and 9.7 percent (by weight of the copolymer) of acrylic acid); ATTANE® 4201 (an ethylene/1-octene copolymer made by The Dow Chemical Company having I₂ of 1 g/10 minutes, a density of 0.912 g/cm³, a melt flow ratio (I₁₀/I₂) of 8.6, a molecular weight distribution (M_w/M_n) of 3.7, and multiple melting peaks); another ethylene/1-octene copolymer made by The Dow Chemical Company having I₂ of about 1 g/10 minutes, a density of 0.902 g/cm³, a melt flow ratio (I₁₀/I₂) of 9.5, a molecular weight distribution (M_w/M_n) of 4.1, and multiple melting peaks); Elvax® 3165 EVA (0.7 MI, 18 percent VA ethylene/vinyl acetate copolymer made by E. I. DuPont de Nemours); and four substantially linear ethylene/1-octene copolymers each having a single melting peak and were produced using constrained geometry catalysis.

Hot tack measurements were performed on a Packforsk testing machine using a seal time of 0.5 seconds, a delay time after seal of 0.2 seconds, a peel speed of 150 mm/sec, and seal pressure of 0.275 MPa. Coextruded films were 2.54 cm (1 inch) wide. Hot tack was recorded in Newtons (N) for the 2.54 cm wide strips. Generally, a hot tackable film means that hot tack strength is achieved quickly after the seal has been performed, as distinguished from heat seal tests, where strength is measured much later.

Heat seal properties of film are described in Packaging Foods With Plastics, by W.A. Jenkins and J.P. Harrington (1991), pp. 32-33. Jenkins and Harrington describe two different kinds of heat seal properties: 1) the strength of the seal after it is made, allowed to cool and then aged for a time (frequently as long as a week), and 2) the strength of the seal immediately after it is made (known as hot tack). Hot tack could be

expressed as a percentage of the ultimate aged heat seal value. To be more definitive, hot tack is the heat seal strength measured 0.1 to 10 seconds after the seal has been applied (that is, while the seal is still warm from the application of the seal). Heat seal strength is measured 8 hours to more than a week after the seal has been applied (that is, after the seal has cooled and aged for a time). Jenkins and Harrington also provide a brief description of the polymers used in packaging on pp. 35-63. The two families of polymers identified by Jenkins and Harrington for having excellent hot tack are ethylene/acid copolymers (for example, ethylene-co-acrylic acid and ethylene-co-methacrylic acid) and ionomers (for example, sodium or zinc ionomers of the ethylene-acid copolymers). Comparative Examples 28 and 29 were representative of the polymers shown by Jenkins and Harrington as industry standard polymers having excellent hot tack performance.

Hot tack was measured for clean seals and is reported in Table 17. Hot tack data for seals contaminated with bacon grease is reported in Table 18.

Table 17

Hot Tack Measured on Clean Nylon Coextruded Films (Newtons)

Heat Seal Temp. (°C)	70	80	90	95	100	105	110	120
Ex. 24	2.7	6.4	4.5	3.9	3.4	NM	3.1	NM
Comp. Ex. 25*	0.6	1.6	2.5	2.2	2.1	NM	1.7	NM
Ex. 26	NM	1.5	5.5	8.4	9.9	10.2	8.3	4.4
Ex. 27	NM	NM	0.2	2	5.6	11.4	9.4	5.7
Comp. Ex. 28*	NM	0.7	1.8	3.8	4.3	4.3	4.5	5.3
Comp. Ex. 29*	NM	1	2	3.2	3.7	3.6	3.5	4.2
Comp. Ex. 30*	NM	0.7	3.2	3.7	3.3	3.5	3	2.9
Comp. Ex. 31*	NM	NM	1.3	2	2.8	3.7	3.2	6.9

NM = Not measured

*Comparative example only; not an example of the invention

The data in Table 17 show that Examples 26 and 27 both had surprisingly high hot tack strength, as compared with comparative examples 28 and 29. Examples 3 and 4 had different densities, and similar I₂, yet

the resultant hot tack performance was the same for these two examples, indicating that the improvement in hot tack performance was not solely attributable to a density difference.

Comparing Ex. 26 ($I_2 = 1$ g/10 min and density = 0.902 g/cm³) with
 5 Comp. Ex. 30 ($I_2 = 1$ g/10 min and density = 0.902 g/cm³), the hot tack performance of Ex. 26 was surprisingly higher by over 175 percent, even though the two polymers had about the same I_2 and density. Similarly, comparing Ex. 27 ($I_2 = 1$ g/10 min and density = 0.910 g/cm³) with Comp.
 10 Ex. 31 ($I_2 = 1$ g/10 min and density = 0.912 g/cm³), the hot tack performance of Ex. 27 was higher by over 200 percent, even though the two polymers had similar I_2 and density.

Comparing Examples 26 and 27 with Comparative Examples 28 and 29 also shows that the hot tack strength for the film of the present invention is higher by at least 90 percent, demonstrating that using the
 15 substantially linear ethylene/ α -olefin copolymers in film structures improved hot tack performance over comparable specialty polymers (Comp. Ex. 20 = Surlyn® 1601 and Comp. Ex. 29 = PRIMACOR® 1410).

Table 18
 Hot Tack Measured on Nylon Coextruded Films

Rubbed with Bacon Grease (in Newtons)								
Seal Temp (°C)	70	80	90	95	100	105	110	120
Ex. 24	3.9	3.3	3.3	3.3	2.6	NM	2.3	NM
Comp. Ex. 25*	NM	2.1	2	1.8	1.3	NM	1.3	NM
Ex. 26	NM	0.3	4.2	5.6	7.3	7.2	4.9	3
Ex. 27	NM	NM	0.1	1.3	4.4	7.1	6.5	4.3
Comp. Ex. 28*	NM	NM	2	1.8	2.4	2.8	3.6	4.7
Comp. Ex. 29*	NM	NM	1.8	2.9	3.4	3.5	4.2	3.6
Comp. Ex. 30*	NM	1.1	1.4	1.1	1.7	2.1	2.7	2.8
Comp. Ex. 31*	NM	NM	NM	0.3	1.1	2	3.2	4.7

NM = Not Measured

*Comparative example only; not an example of the invention

25 Table 18 demonstrates that the novel films made using substantially linear ethylene polymer maintained superior hot tack performance, even when sealed through contaminants, for example, bacon grease.

Tables 19 and 20 summarize data for hot tack and heat seal formed using a Topwave tester using the same coextruded films from Example 27 and Comparative Examples 28 and 31.

Hot tack conditions used were: dwell time of 0.5 seconds, delay time after seal of 0.2 seconds, peel speed of 150 mm/s, and seal pressure of 0.27 MPa. Hot tack was recorded in Newtons (N) for the 2.54 cm wide strips.

Heat seal conditions used were: dwell time of about 0.5 seconds, delay time after seal greater than 24 hours, and seal pressure of about 0.27 MPa. These heat sealed samples were pulled on an Instron Tensiometer at a peel speed of 50 mm/min and the heat seal values were recorded in Newtons (N) for the 2.54 cm wide strips.

Table 19

Hot Tack of Nylon Coextruded Films On Topwave Tester (Newton)			
Temp. (°C)	Example 27	Comp. Ex. 28*	Comp. Ex. 31*
90	0	2.0	2.0
95	0.3	4.0	3.1
100	4.8	4.7	3.6
105	10.1	4.6	4.3
110	12.0	4.8	4.8
115	10.2	NM	5.6

15

Table 20

Heat Seal of Nylon Coextruded Films On Topwave Tester (Newton)			
Temp. (°C)	Example 27	Comp. Ex. 28*	Comp. Ex. 31*
90	0.3	5.3	0.9
95	15.3	15.8	2.6
100	25.0	21.9	19.3
105	34.6	22.8	30.6
110	36.8	23.6	NM
115	39.0	NM	34.1

The data in Tables 19 and 20 shows that the novel substantially linear ethylene/ α -olefin copolymers used as sealants in coextruded films had approximately twice the ultimate hot tack strength and equivalent or superior heat seal strengths relative to specialty polyolefins (for
5 example, Comp. Ex. 28) and ULDPE (for example, Comp. Ex. 31), respectively.

Hot blown coextruded films were made using nylon, an adhesive layer, and a sealant layer. The blown film was made using the same equipment as described in Example 1, except that PRIMACOR® 1410 adhesive resin, an
10 ethylene/acrylic acid copolymer made by The Dow Chemical Company, was substituted as the adhesive resin.

The sealant layers included Surlyn® 1601 ionomer, a sodium ionomer of ethylene/methacrylic acid (EMAA) copolymer from E. I. DuPont de Nemours; ATTANE® 4201, an ethylene/1-octene copolymer made by The Dow
15 Chemical Company; Tafmer® A 4085, an ethylene/1-butene copolymer from Mitsui Petrochemical; and two novel substantially linear ethylene/1-octene copolymers using constrained geometry catalyst polymerization, as described herein.

Heat seal and hot tack were measured for clean seals. The hot tack
20 measurements were performed on a Topwave testing machine using seal time of 0.5 seconds, delay time after seal of 0.2 seconds, peel speed of about 150 mm/sec, and seal pressure of 0.275 MPa. Coextruded films were 2.54 cm (1 inch) wide. Hot tack was recorded in Newtons (N) for the 2.54 cm wide strips and is reported in Table 21.

25 The heat seal measurements were performed on a Topwave testing machine using seal time of 0.5 sec and seal pressure of 0.275 MPa. After a delay time of greater than 24 hours, the samples were peeled on an Intron Tensiometer at a peel speed of 50 mm/min. Coextruded films were 2.54 cm (1 inch) wide. Heat seal strength was recorded in Newtons (N) for
30 the 2.54 cm wide strips and is reported in Table 22.

Table 21

Hot Tack Measured on Clean Nylon Coextruded Films (Newtons)

Seal Temp. (°C)	70	75	80	85	90	95	100	105	110	115
Ex. 32	NM	0.8	1.3	2.6	4.9	11.6	11.4	9.4	8.2	6.4
Comp. Ex. 33*	1.2	5.7	6.4	5.7	4.4	4.2	3.5	3.5	NM	NM
Ex. 27	NM	NM	NM	NM	0.9	1.1	3.4	10.6	10	8.1
Comp. Ex. 28*	NM	NM	NM	0.6	1.6	2.1	3.8	4.2	4.3	4.8
Comp. Ex. 31*	NM	0.6	1	2.3	2.3	3.1	3.7	4.5	4.7	7.4

NM=Not Measured

*Comparative example only; not an example of the invention

5

As the data in Table 21 demonstrate, Example 32 had a maximum hot tack strength of about 11.6 N as compared with Comparative Example 33, which had a maximum hot tack strength of about 6.4 N, representing an increase of at least about 80 percent in hot tack performance.

- 10 Surprisingly, the density difference between Ex. 32 and Comp. Ex. 33 was about the same as the density difference between Ex. 26 and Ex. 27, which had about the same ultimate hot tack strengths, which means that the expected hot tack strengths of Ex. 32 and Comp. Ex. 33 should have also been about the same, contrary to that discovered for structures of the
- 15 invention made using the novel substantially linear ethylene polymers.

Table 22

Heat Seal Measured on Clean Nylon Coextruded Films

Heat Seal Temp. (°C)	70	75	80	85	90	95	100	105	110	115
Ex. 32	NM	0.4	1.7	13.3	25.4	34.3	33.4	35.1	38.3	38.3
Comp. Ex. 33*	6.7	26.2	33.4	31.6	32.9	35.6	35.6	37.7	38.3	36.9
Ex. 27	NM	NM	NM	NM	0.2	2.5	23.6	34.7	38.3	40.5
Comp. Ex. 28*	NM	NM	NM	0.2	2.4	5.8	10.2	16.9	16.0	23.1
Comp. Ex. 31*	NM	0.1	0.2	0.4	1.0	4.9	24.9	31.1	35.6	39.1

NM = Not Measured

- 20 *Comparative example only; not an example of the invention

As the data in Tables 21 and 22 show, the maximum heat seal strength for Example 32 and for Comparative Example 33 were about the same (about 38.3 N). The difference in hot tack and heat seal testing was the length of delay time after the seal was formed until the seal was peeled open. Hot tack was measured less than a second after the seal was formed, and heat seal was measured more than 24 hours after the seal was formed. Equivalent maximum heat seal strengths for Example 32 and Comparative Example 33 means that the expected hot tack strength should also be about the same, contrary to that discovered for structures of the invention using the novel substantially linear ethylene polymers.

We claim:

1. A film suitable for use in packaging and wrapping food, beverages and nonfood articles comprising at least one layer of at least one substantially linear ethylene polymer characterized as
5 having:
 - (A) a melt flow ratio, $I_{10}/I_2 \geq 5.63$,
 - (B) a molecular weight distribution, M_w/M_n , defined by the equation: $M_w/M_n \leq (I_{10}/I_2) - 4.63$, and
 - (C) a critical shear rate at onset of surface melt fracture of at
10 least 50 percent greater than the critical shear rate at the onset of surface melt fracture of a linear ethylene polymer having about the same I_2 and M_w/M_n .
- 15 2. The film of Claim 1 wherein the film is a shrink film structure.
3. The film of Claim 1 wherein the film is an oriented shrink film structure.
4. The film of Claim 1 wherein the film is a biaxially oriented
20 film structure.
5. The film of Claim 1 wherein the film is a hot tack film structure.
- 25 6. The film of Claim 1 wherein the film is a skin packaging film structure.
7. The film of Claim 1 wherein the film is a stretch film structure.
30
8. The film of Claim 1 wherein the film is a vacuum wrap film structure.
9. The film of Claim 1 wherein the film comprises at least one hot
35 tack layer.

10. The film of Claim 1 wherein the film comprises at least one oriented film layer.

11. The film of Claim 1 wherein the film comprises at least one
5 biaxially oriented film layer.

12. The film of Claim 1 wherein the film is a film structure made using a hot blown simple bubble film manufacturing technique.

10 13. The film of Claim 1 wherein the film is a film structure made using a double bubble or trapped bubble film manufacturing technique.

14. The film of Claim 1 wherein the film is a film structure made using a tenter frame or a high blow-up ratio film manufacturing technique.
15

15. The film of Claim 1 wherein the film is a multilayer film structure.

16. The film of Claim 1 wherein the substantially linear ethylene
20 polymer is further characterized as having:

(D) a density greater than 0.85 g/cm³, and

(E) a melt index (MI) as measured by ASTM D-1238, Condition 190°C/2.16 kg from 0.01 g/10 minutes to 10 g/10 minutes.

25 17. The film of Claim 1 wherein said film is in the form of a package or bag.

18. The film in Claim 1 wherein the substantially linear ethylene polymer is an ethylene/ α -olefin copolymer.
30

19. A method of manufacturing shrink film for use in packaging and wrapping food, beverages and nonfood articles comprising the steps of:

(A) extruding at least one substantially linear ethylene
35 polymer into at least one layer of an extrudate, wherein

the substantially linear ethylene polymer is characterized as having:

(i) a melt flow ratio, $I_{10}/I_2 \geq 5.63$,

(ii) a molecular weight distribution, M_w/M_n , defined by the equation: $M_w/M_n \leq (I_{10}/I_2) - 4.63$, and

(iii) a critical shear rate at onset of surface melt fracture of at least 50 percent greater than the critical shear rate at the onset of surface melt fracture of a linear ethylene polymer having about the same I_2 and M_w/M_n ,

(B) passing the extrudate of (A) through an annular die to form a tubular film.

20. A method of manufacturing oriented film for use in packaging and wrapping food, beverages and nonfood articles comprising the steps of:

(A) extruding at least one substantially linear ethylene polymer into at least one layer of an extrudate, wherein the substantially linear ethylene polymer is characterized as having:

(i) a melt flow ratio, $I_{10}/I_2 \geq 5.63$,

(ii) a molecular weight distribution, M_w/M_n , defined by the equation: $M_w/M_n \leq (I_{10}/I_2) - 4.63$, and

(iii) a critical shear rate at onset of surface melt fracture of at least 50 percent greater than the critical shear rate at the onset of surface melt fracture of a linear ethylene polymer having about the same I_2 and M_w/M_n ,

(B) passing the extrudate of (A) through an annular die to form a primary tube film,

(C) heating the primary film tube, and

(D) orienting the heated primary film tube.

21. The method of Claim 20 wherein the orientation is accomplished using a double bubble technique, a tenter frame, by blowing-up the primary film tube to a blow-up ratio of at least 2.5:1 or any combination.

5

22. The method of Claim 20 wherein the primary tube film is irradiated before the orientation step (D).

23. The method of Claim 20 wherein the primary tube film is
10 irradiated after the orientation step (D).

24. A method of manufacturing hot tack film comprising the steps of:

15 (A) extruding at least one substantially linear ethylene polymer into an extrudate, wherein the substantially linear ethylene polymer is characterized as having:

- (i) a melt flow ratio, I_{10}/I_2 , ≥ 5.63 ,
- 20 (ii) a molecular weight distribution, M_w/M_n , defined by the equation: $M_w/M_n \leq (I_{10}/I_2) - 4.63$, and
- (iii) a critical shear rate at onset of surface melt fracture of at least 50 percent greater than the critical shear
25 rate at the onset of surface melt fracture of a linear ethylene polymer having about the same I_2 and M_w/M_n , and
- (B) passing the extrudate of (A) through an annular die to form an outer layer of the film.

30

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 93/09821

A. CLASSIFICATION OF SUBJECT MATTER IPC 5 C08J5/18 //C08J5/18,C08L23/08		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) IPC 5 C08J C08F C08L		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 416 815 (THE DOW CHEMICAL COMPANY) 13 March 1991	1,3,4, 12-14, 16,18,19
Y	see page 11, line 32 - page 12, line 48; claim 31; figures 15-17; examples 12-32; table 2 ---	2-15, 19-23
X	WO,A,92 14784 (EXXON CHEMICAL PATENTS INC.) 3 September 1992 see page 3, line 30 - page 10, line 30; claims 1,4,5,8,12,15,17 ---	1,3,4, 9-18,20, 24
Y	EP,A,0 452 920 (MITSUI PETROCHEMICAL IND., LTD.) 23 October 1991 see page 2, line 20 - line 54; claim 1 see page 5, line 1 - page 6, line 40 see page 14, line 37 - page 16, line 1 --- -/--	1,12-14, 16-18
<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "Z" document member of the same patent family		
Date of the actual completion of the international search 17 February 1994		Date of mailing of the international search report 14. 03. 94
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer Derz, T

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 93/09821

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP,A,0 495 099 (MITSUI PETROCHEMICAL INDUSTRIES, LTD.) 22 July 1992 see page 3, line 15 - line 40; claims 1,7 see page 6, line 20 - line 37 see page 20, line 16 - line 57 ---	1,5,9, 16,18
Y	GB,A,2 206 890 (W R GRACE & CO - CONN) 18 January 1989 see page 11, line 32 - page 14, line 22; claims 1,5,15,20 ---	6,8,9, 15,22,23
Y	US,A,5 132 074 (ISOZAKI ET AL.) 21 July 1992 see column 3, line 27 - column 4, line 15; claim 1; example 1 ---	2-4,7, 9-14, 19-21
Y	US,A,4 243 619 (UNION CARBIDE CORPORATION) 6 January 1981 see column 2, line 1 - column 5, line 39; claims 1-3,6,10,25 see column 17, line 42 - column 18, line 22 ---	4,10-14, 17,18, 20,21
P,X	WO,A,93 08221 (THE DOW CHEMICAL COMPANY) 29 April 1993 see page 4, line 2 - page 11, paragraph 1; claims 2,8,10,27-30; examples 5,20; tables 2,3 ---	1,4,5, 9-14,16, 18,20, 21,24
P,A	WO,A,93 07210 (THE DOW CHEMICAL COMPANY) 15 April 1993 see page 3, line 5 - page 7, line 22; claims 1,3,9,10,13 ---	1,12-15, 17-19
A	EP,A,0 141 597 (MITSUI PETROCHEMICAL INDUSTRIES) 15 May 1985 see page 5, line 1 - page 8, line 8; claim 1 see page 21, line 16 - line 29 ---	1,11-16, 18,19
T	MODERN PLASTICS INTERNATIONAL vol. 23, no. 8, August 1993, LAUSANNE CH pages 40 - 41 DON SCHWANK 'Single-site metallocene catalysts yield tailor-made polyolefin resins' -----	1-4,6-8, 12-14, 18,19

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 93/09821

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A-0416815	13-03-91	AU-B-	645519	20-01-94
		AU-A-	6203990	07-03-91
		CA-A-	2024333	01-03-91
		JP-A-	3163088	15-07-91
		CN-A-	1049849	13-03-91

WO-A-9214784	03-09-92	EP-A-	0575465	29-12-93

EP-A-0452920	23-10-91	AU-B-	640559	26-08-93
		AU-A-	1286692	21-05-92
		AU-A-	4011893	26-08-93
		AU-B-	624289	04-06-92
		AU-A-	7502991	24-10-91
		CN-A-	1055935	06-11-91
		JP-A-	4213305	04-08-92
		KR-B-	9311666	16-12-93
		JP-A-	4213309	04-08-92
JP-A-	4213306	04-08-92		

EP-A-0495099	22-07-92	JP-A-	2173014	04-07-90
		JP-A-	2173016	04-07-90
		JP-A-	2173015	04-07-90
		WO-A-	9007526	12-07-90
		JP-A-	2276807	13-11-90
		US-A-	5218071	08-06-93

GB-A-2206890	18-01-89	AU-A-	1850988	05-01-89
		JP-A-	1105739	24-04-89
		US-A-	5033253	23-07-91

US-A-5132074	21-07-92	NONE		

US-A-4243619	06-01-81	AT-B-	376226	25-10-84
		AT-B-	376227	25-10-84
		AT-B-	375948	25-09-84
		AU-B-	529734	16-06-83
		AU-A-	4565779	18-10-79
		CA-A-	1131838	14-09-82
		EP-A,B	0006110	09-01-80
		JP-A-	54154466	05-12-79

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 93/09821

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-4243619		JP-B- 62015327	07-04-87
WO-A-9308221	29-04-93	US-A- 5272236	21-12-93
		US-A- 5278272	11-01-94
WO-A-9307210	15-04-93	US-A- 5250612	05-10-93
EP-A-0141597	15-05-85	JP-B- 3036042	30-05-91
		JP-A- 60088016	17-05-85
		CA-A- 1240097	02-08-88
		US-A- 4668752	26-05-87